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- I THE ANALYTICAL APPLICATIONS OF  
2,2' - PYRIDILMONOXIME
- II THE ANALYTICAL APPLICATIONS OF  
2,2' - DIQUINOLYL KETOXIME

BY

SAM STUPAVSKY

A Dissertation

Submitted to the Faculty of Graduate Studies through the  
Department of Chemistry in Partial Fulfillment of the  
Requirements for the Degree of Doctor of  
Philosophy at the University of Windsor

Windsor, Ontario  
1971

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## ABSTRACT

### PART I

#### THE ANALYTICAL APPLICATIONS OF 2,2' - PYRIDILMONOXIME

The reactions of metals with 2,2' - pyridilmonoxime have been studied and the reagent has been applied to the spectrophotometric determination of palladium and cobalt. For palladium and cobalt, the effects due to pH, time, solvents, reagent concentration and diverse ions have been studied. The palladium and cobalt chelates have been isolated and characterized. Based upon spectral evidence, the 2,2' - pyridilmonoxime, m.p. 193-194°C, has been assigned the  $\alpha$  configuration.

### PART II

#### THE ANALYTICAL APPLICATIONS OF 2,2' - DIQUINOLYL KETOXIME

The reagent 2,2' - diquinolyl ketoxime has been synthesized and its reactions with metals have been studied. It forms coloured water-insoluble complexes with cobalt, palladium, copper, gold and nickel. The cobalt and palladium complexes possessed suitable analytical properties and procedures were developed for the determination of cobalt and palladium.

## ACKNOWLEDGEMENTS

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## GENERAL INTRODUCTION

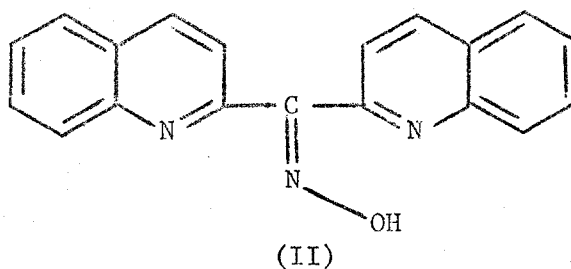
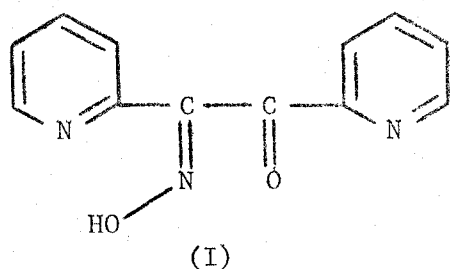
Of the various methods of trace analysis, spectrophotometric methods are the most widely used. The popularity of spectrophotometry in the determination of trace and minor constituents arises from its modest apparative requirements, the possibility of its use by the average analyst, a sensitivity adequate for many purposes, and an accuracy often as good as, if not better than any other method in its range.

Spectrophotometric methods involve the measurement of the intensity of the colour of the constituent to be determined. Substances which are colourless or only faintly coloured may be analyzed by adding a substance which will react with them to form an intensely coloured compound.

Reagents used for the spectrophotometric determination of metallic elements may be either inorganic or organic. Organic determination forms are superior to the inorganic because of better sensitivity or selectivity or both. The formation of a greater variety of metal complexes (notably chelate compounds) by organic reagents, the greater choice of chromogenic groups in organic compounds, and the possibility of suitably modifying organic molecules, all contribute to the more versatile character of organic reagents as compared to the inorganic.

Oximes of many heterocyclic organic compounds have been widely used as spectrophotometric reagents. Pyridine oximes have been especially useful because of the strong coordinating ability of the nitrogen donor atom.

The purpose of the present work was to investigate the organic reagents, 2,2' - pyridilmonoxime (I) and 2,2' - diquinolyl ketoxime (II) with a view of applying them to the determination of trace amounts of metals.



Spectrophotometric methods have been developed for palladium and cobalt utilizing 2,2' - pyridilmonoxime and 2,2' - diquinolyl ketoxime.

## THEORY

If a beam of white light is allowed to pass through a glass cuvette filled with liquid, the emergent radiation will be less powerful than that entering. The diminuation in power may be approximately equal over the whole wavelength range, or it may be of different extent for different colours. The loss is due in part to reflections at the surfaces and in part to scattering by any suspended particles present, but primarily by the absorption of radiant energy by the liquid. To the analytical chemist, the importance of coloured solutions lies in the fact that the radiation which is absorbed is characteristic of the material doing the absorbing and the degree of the absorption may be used as a measure of the concentration.

There are two fundamental laws related to the absorption of monochromatic radiant energy by homogeneous, transparent systems. Lambert's Law (Bouguer's Law) states that when a beam of parallel monochromatic radiation enters an absorbing medium at right angles to plane, parallel surfaces of the medium, each infinitesimally small layer of the medium decreases the intensity of the beam entering that layer by a constant fraction. Beer's Law states that the intensity of a beam of parallel, monochromatic radiation decreases exponentially as the concentration of the absorbing material increases. The two laws combined can be expressed mathematically by the following relationship:

$$\log \frac{I_0}{I} = a b c = A$$

where  $I_0$  = intensity of the incident light beam;  $I$  = intensity of the transmitted light beam;  $A$  = absorbance;  $a$  = absorptivity;  $b$  = light path length;  $c$  = concentration of the coloured species. If the concentration is expressed in moles per litre and the light path in centimetres,  $a$  becomes the molar extinction coefficient or molar absorptivity and is commonly designated by  $\epsilon$ .

There are no known exceptions to the Lambert Law so that non-conformity of an absorbing system to the Beer - Lambert Law is taken as a failure of the Beer Law to adequately express the behaviour of the system. Three kinds of effects can be distinguished which may cause deviations: chemical and/or physical (non-instrumental) effects, instrumental effects and a combination of chemical and instrumental effects. Many workers have studied these effects, the most recent being Buijs and Maurice (1).

When the absorbance of a substance is plotted against wavelength an absorption spectrum is obtained. Many coloured species have unique absorption spectra in the visible region and in many cases one or more maxima may be present in the absorption curves. For spectrophotometric measurements it is advisable to select a band of radiation which forms a part of an absorption plateau, since the effect of the temperature of the solution and the influence of slight variations in the wavelength are then reduced to a minimum. Moreover, under these conditions Beer's Law and the additivity of absorbances are most likely to remain valid.

In spectrophotometric trace analysis, a knowledge of the sensitivity of the colour reaction employed is of paramount importance, and it is

necessary to have a simple method available for the expression of the sensitivity. For comparative purposes the molar absorptivity at the wavelength of maximum absorption is used as a measure of sensitivity. For a particular metal ion, the greater the molar absorptivity, the more sensitive is the method. The Sandell sensitivity (2) is defined as the number of micrograms of element, converted to the coloured product, which in a column of solution having a cross section of  $1 \text{ cm}^2$  shows an absorbance of 0.001. Both the molar absorptivity and the Sandell sensitivity are usually quoted when describing the sensitivity of a particular spectrophotometric method.

If absorptancy (100 - percent transmittance) is plotted against the logarithm of the concentration a Ringbom plot is obtained (3,4). If a sufficient range of concentrations has been covered, an S - shaped curve always results. If the system follows Beer's Law, the point of inflection occurs at 37 percent transmittance; if not, the inflection is at some other value but the general form of the curve is the same. The curve generally has a considerable region which is nearly straight. The extent of the straight line portion indicates directly the optimum range of concentrations for the particular spectrophotometric analysis.

Many spectrophotometric methods for metals depend upon the formation of coloured complex ions or molecules. It is frequently important to know the molar ratio of metal to reagent in the complex. This is normally determined from spectrophotometric data by two different procedures: the mole - ratio method introduced by Yoe and Jones (5) and the method of continuous variations attributable to Job (6) and modified by Vosburgh and Cooper (7).

In the mole - ratio method, the absorbances are measured for a series of solutions which contain varying amounts of one constituent with a constant amount of the other. A plot is prepared of absorbance as a function of the moles of reagent to moles of metal ion. This is expected to give a straight line from the origin to the point where equivalent amounts of the constituents are present. The curve will then become horizontal, because all of one constituent is used up and the addition of more of the other constituent can produce no more of the absorbing complex.

The method of continuous variations requires a series of solutions of varying mole fractions of the two constituents while their sum is kept constant. The absorbance is plotted against the mole fraction of one of the constituents. The resulting curve will show a maximum corresponding to that in the complex.

Organic reagents used in chemical analysis may be defined as those carbon - containing substances which by some form of interaction enable other ions or molecules to be detected or determined (8). An important class of organic reagents are those which form chelates with metal ions.

Metal chelates are a type of coordination compound in which a metal ion combines with a polyfunctional base capable of occupying two or more positions of the coordination sphere of the metal ion to form a cyclic compound. The functional groups of the chelating agent must be so situated that they permit the formation of a stable ring (usually 5 or 6 membered).

Chelating agents may be classified according to the charge type of the basic groups present. If the basic groups of the reagent are uncharged, positively charged metal chelates are formed. If the reagent has both an acidic and basic group, neutral chelates usually result. The presence of multiple negative charge on chelating agents results in negatively charged chelates. The reagents 2,2' - pyridilmonoxime and 2,2' - diquinolyl ketoxime contain both an acidic group and a basic group and hence formed neutral chelates with palladium and cobalt.

A most important property of many metal - organic complexes from the standpoint of trace analysis is their extractability by organic solvents not miscible with water. Solvent extraction permits the determination of water insoluble coloured species and in many cases improves both the selectivity and sensitivity. The systems presented in this dissertation involved the extraction of the metal chelates into organic solvents. The theory and applications of solvent extraction in trace metal analysis have been discussed by several authors (9-11).

The reliability of an analytical method is normally expressed in terms of precision and accuracy. The accuracy of a determination may be defined as the concordance between it and the true or most probable value. Precision may be defined as the concordance of a series of measurements of the same quantity. Accuracy expresses the correctness of a measurement and precision the reproducibility of a measurement. Precision always accompanies accuracy, but a high degree of precision does not imply accuracy.

To obtain a quantitative measure of precision corresponding to a



given method and a set of conditions, several parameters can be used, e.g., the range of the results, the mean deviation from the mean, the standard deviation. The aim is to determine, from a finite number of results, the variability that would be observed in an infinite number of results, i.e., an estimate is made of the true variability. The parameter used should therefore have as good a precision and bias as possible, and the best parameter is variance. For a homogeneous set of  $n$  results, the estimate,  $V$ , of the true variance is given by the equation:

$$V = \frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n-1}$$

Where  $\bar{X}$  is the mean result. The square root of the variance gives an estimate,  $s$ , of the true standard deviation  $\sigma$ . The standard deviation ( $s$ ) of analytical results is now the most common parameter for the quantitative expression of precision.

PART I

THE ANALYTICAL APPLICATIONS OF 2,2' - PYRIDIL -

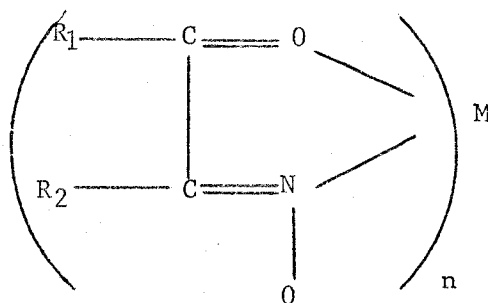
MONOXIME

# CHAPTER I

## INTRODUCTION

The use of  $\alpha$ -keto oximes as analytical reagents is very limited. These reagents containing the  $\begin{array}{c} \text{C} \quad \text{C} \\ || \quad || \\ \text{O} \quad \text{N} \\ \quad \quad \text{OH} \end{array}$  atomic grouping are known to

form coloured (water-insoluble) precipitates, soluble in chloroform with many metal ions (12). Iron, palladium, cobalt, nickel, copper, zinc, cadmium and mercury are some of the metals which form complexes with  $\alpha$ -keto oximes. The ligands are monoanions and the metal is bound through an oxygen and a nitrogen atom in a five-membered ring (III).



(III)

The reagents belonging to this class include isonitrosoacetone, isonitrosoacetophenone, biacetylmonoxime,  $\alpha$ -benzilmonoxime and the monoxime of di- $\alpha$ -naphthylglyoxal. The reactions of metals with  $\alpha$ -benzilmonoxime have been extensively studied (13,14) and the reagent has been applied to the spectrophotometric determination of cobalt (15) and palladium (16). Isonitrosoacetophenone has been applied to the spectrophotometric determination of palladium (17) and the monoxime of di- $\alpha$ -naphthylglyoxal has been applied to the spectrophotometric determination of cobalt (18).

In the present work the reactions of metals with 2,2' - pyridilmonoxime (an analogue of  $\alpha$ -benzilmonoxime) were investigated with a view of applying the reagent to the spectrophotometric determination of various metals. The reagent formed analytically useful complexes with palladium and cobalt and spectrophotometric methods for these two metals were developed (19,20).

## CHAPTER II

### SYNTHESIS AND PROPERTIES OF 2,2' - PYRIDIL MONOXIME

#### AND ITS REACTIONS WITH METALS

##### A. INTRODUCTION

Pyridine ketoximes have found wide applications in trace metal analysis. In the present work an unsymmetrical pyridine ketoxime with a keto group as an additional coordinating site was synthesized and studied as an analytical reagent. The reagent was synthesized by the reaction of 2,2' - pyridil with hydroxylamine hydrochloride and its properties were studied. The reactions of metals with 2,2' - pyridilmonoxime were investigated with a view of applying the reagent to the analysis of trace amounts of metals. The reagent was found to be highly selective and sensitive for palladium and cobalt.

##### B. EXPERIMENTAL

###### 1) Synthesis of 2,2' - Pyridilmonoxime

To 21.2g (0.1 mole) of 2,2' - pyridil dissolved in a 50 : 50 mixture of 95% ethanol and pyridine was added 7.0g (0.1 mole) of hydroxylamine hydrochloride. The solution was heated on the steam bath for thirty minutes, cooled and then poured into 200 ml of cold distilled water. The mixture was stirred for 15 minutes and filtered. The precipitate was washed thoroughly with distilled water and recrystallized from 95% ethanol. There was obtained 15.1g (66% yield) of white crystals m.p. 193 - 194°C . Analysis calculated for  $C_{12}H_9N_3O_2$  : C, 63.43%; H, 3.99%; N, 18.49%. Found: C, 63.26%; H, 3.96%; N, 18.61%. Carbon, hydrogen and nitrogen analyses were done by the Spang Micro-analytical Laboratory, Ann Arbor, Michigan.

## 2) Apparatus

Nuclear Magnetic Resonance spectra were obtained, using 10% W/V solutions in deuterated dimethylsulfoxide with TMS as the internal standard, on a JNM -C - 60 HL spectrometer. Infrared spectra were obtained with a Beckman IR - 10 and a Beckman IR - 12 using 1% potassium bromide discs. Ultraviolet spectra were obtained with a Beckman DB spectrophotometer equipped with a Sargent SRL recorder. Melting points were obtained with a Fisher - Johns Melting Point Apparatus. A Sargent Model LS pH meter was used for PH measurements.

## 3) Chemicals

2,2' - Pyridil was obtained from Aldrich Chemical Company.

Hydroxylamine Hydrochloride, analytical reagent grade from Mallincrodt Chemical Works.

Pyridine and chloroform, A.C.S. grades were used.

## 4) Reagent Solutions

For the palladium study a 1% W/V solution in 0.6 M hydrochloric acid was used. For the other studies a 1% W/V solution in 95% ethanol was used.

## 5) Standard Solutions

A stock solution of palladium was prepared by dissolving anhydrous palladium (II) chloride (Fisher Scientific) in concentrated hydrochloric acid, diluting to one litre with distilled water and standardizing with 2,2' - dipyridyl ketoxime (21). A stock solution of copper was prepared by dissolving pure copper wire in 1 : 1 nitric acid and diluting to volume with distilled water. A stock solution of gold was prepared by dissolving  $\text{H Au Cl}_4 \cdot 3\text{H}_2\text{O}$  (Fisher Scientific) in distilled water and

standardizing with hydroquinone (22). A stock solution of iron was prepared by dissolving pure iron wire (Fisher Scientific) in 1:1 hydrochloric acid and diluting to volume with distilled water. A stock solution of nickel was prepared by dissolving pure nickel powder in 1:1 nitric acid and diluting to volume with distilled water. A stock solution of cobalt was prepared by dissolving ultra-pure cobalt metal (Research Inorganic Chemical Comp. Sun Valley, California) in aqua regia, evaporating to near dryness and diluting to volume with distilled water. A stock solution of manganese was prepared by dissolving  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  in distilled water and diluting to volume.

Standard solutions of all of the metals were prepared by appropriate dilutions of the stock solutions.

6) Procedure for the study of the reactions of metals with 2,2' - Pyridilmonoxime

An aliquot of the metal ion was transferred to a 100-ml beaker. To the acidified solution was added five ml of reagent solution. The pH was adjusted with dilute potassium hydroxide or hydrochloric acid. The colour was allowed to develop for 15 minutes and the solutions were diluted to 50.0 ml and the spectra recorded. The palladium and cobalt chelates were extracted into chloroform and diluted to 25.0 ml in glass - stoppered graduated cylinders before spectral measurements were made.

7) Isolation of the Palladium chelate

Two grams of oxime were dissolved in 100 ml of water by the addition of dilute hydrochloric acid. After dissolution was complete the pH was adjusted to 1 by the dropwise addition of dilute potassium hydroxide. A solution of palladium chloride corresponding to 25 mg palladium was prepared and the pH was adjusted to 1. The palladium solution was slowly

added to the oxime solution which was stirred with a magnetic stirrer. After the solutions were completely mixed, the resulting mixture was stirred for approximately five minutes after which a precipitate started to form. The precipitate was digested for thirty minutes on the steam bath and filtered through a medium porosity glass crucible. The precipitate was washed thoroughly with hot distilled water and dried overnight at 150°C. Analysis calculated for  $\text{Pd} (\text{C}_{12}\text{H}_8 \text{N}_3 \text{O}_2)_2$  : C, 51.58%; H, 2.89%; Pd, 19.04%. Found: C, 51.32%; H, 2.92%; Pd, 19.18%. Carbon and hydrogen analyses were done by Spang Microanalytical Laboratory, Ann Arbor, Michigan. The palladium was determined gravimetrically by ignition to the metal. A few drops of formic acid were also added to eliminate any palladium (II) oxide formed.

#### 8) Isolation of the Cobalt Chelate

Five g of oxime were dissolved in 200 ml of hot ethanol by the addition of a few drops of dilute hydrochloric acid. To the oxime solution was added a solution containing 100 mg of cobalt. The pH was adjusted to 5 and the mixture was stirred for 10 minutes. The precipitate was filtered through a medium porosity glass crucible and thoroughly washed with hot water. The chelate was dried overnight at 150°C. Analysis calculated for  $\text{Co} (\text{C}_{12}\text{H}_8\text{N}_3\text{O}_2)_3$  : C, 58.62%; H, 3.28%; Co, 7.99%. Found: C, 58.42%; H, 3.51%; Co, 7.91%. Carbon and hydrogen analyses were done by Midwest Microlab Inc., Indianapolis, Indiana. The cobalt was determined gravimetrically by ignition to the oxide (23).



### C. RESULTS AND DISCUSSION

#### 1) Properties of 2,2' - Pyridilmonoxime

The oxime is insoluble in water, chloroform, methylene chloride and benzene. It is slightly soluble in ethanol. The oxime is soluble in dilute acids and dimethyl sulfoxide. Solutions in ethanol are colourless, whereas solutions in dilute hydrochloric acid are light yellow in colour.

The ultraviolet spectrum of 2,2' - pyridilmonoxime (in 95% ethanol) is shown in Fig. 1. The oxime has maxima at 271 nm and 238 nm with molar absorptivities of  $1.21 \times 10^4$  and  $1.67 \times 10^4$  moles<sup>-1</sup> cm<sup>-1</sup> respectively.

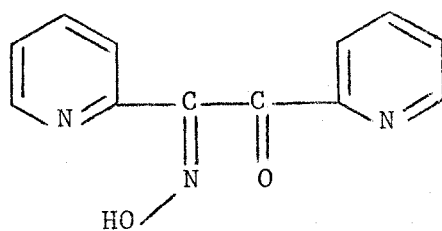
In the infrared the oxime exhibits strong absorption at the following frequencies (in cm<sup>-1</sup>): 3140, 3060, 2800, 1695, 1626, 1582, 1468, 1432, 1272, 1231, 1145, 1090, 1036, 1003, 993, 957, 935, 808, 785, 745, 648, 619, 403 and 319.

The chemical shift of the oxime proton in 10% W/V solution in dimethyl sulfoxide was 11.78 ppm relative to tetramethylsilane.

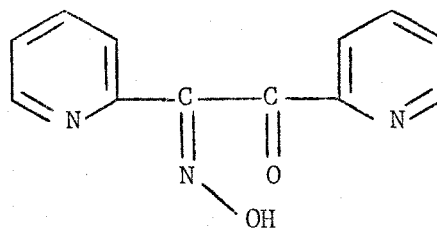
#### 2) Structure of 2,2' - Pyridilmonoxime

Unsymmetrical monoximes can exist in two isomeric forms. They are designated either by  $\alpha$  and  $\beta$  or anti and syn. The two isomeric forms of 2,2' - pyridilmonoxime are represented by structures (IV) and (V).

Synthetic procedures



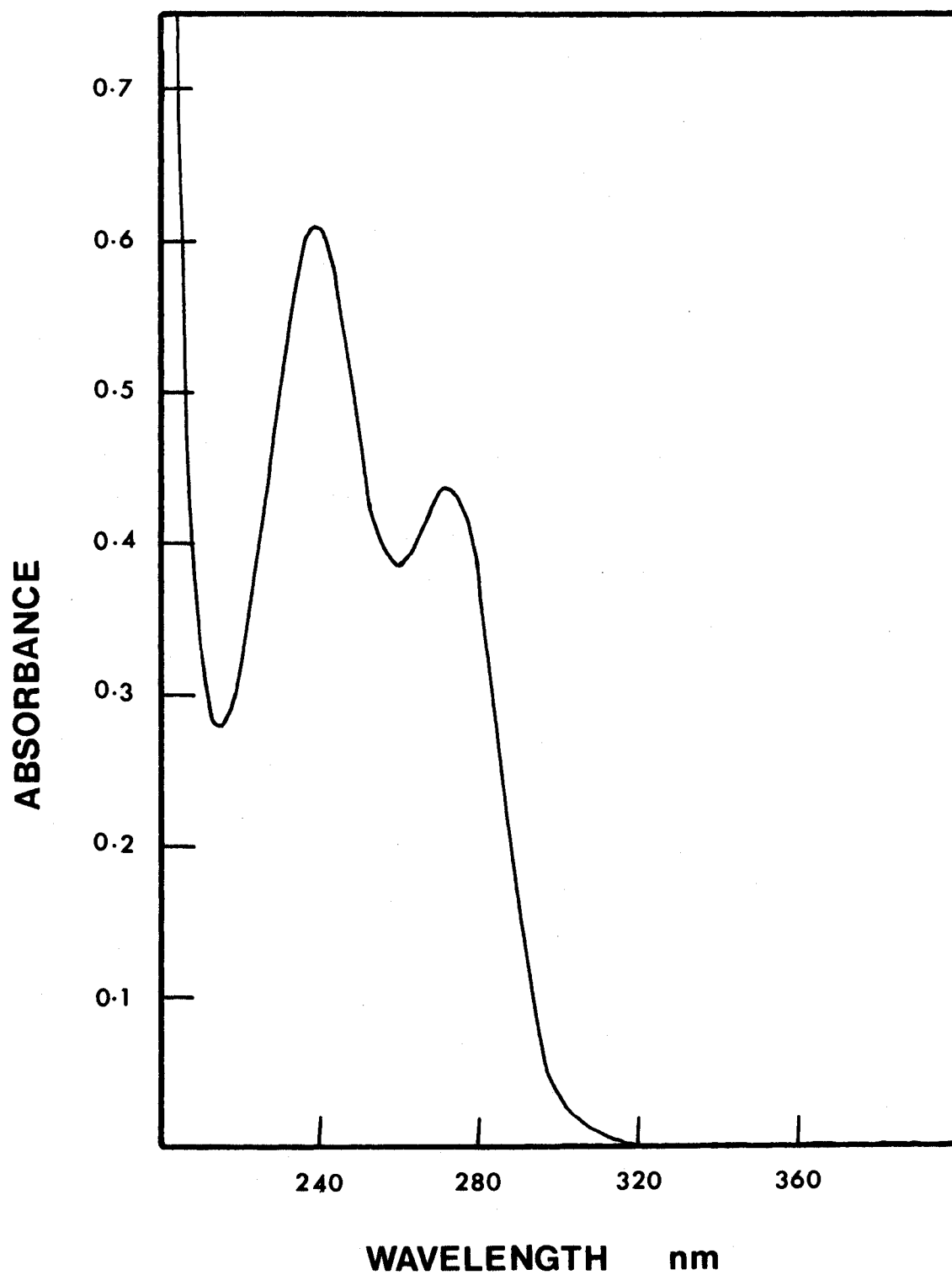
(IV)  
 $\alpha$



(V)  
 $\beta$

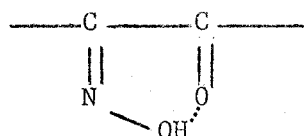


FIGURE 1



yield one or the other or in many cases both of the isomers. When using a new organic reagent, it is important to know its structure and purity. Infrared and NMR spectroscopy were used to investigate the structure and purity of 2,2' - pyridilmonoxime.

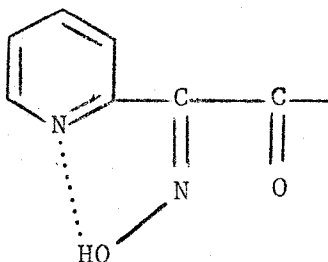
The synthesis of 2,2' - pyridilmonoxime has been reported twice in the literature. Sadler and Pitman (24) reported a monoxime of 2,2' - pyridil, m.p. 207°C as a by-product (1.4% yield) in the synthesis of  $\alpha$  and  $\beta$  isomers of 2,2' - pyridil - dioxime. Sadler (25) in a later communication assigned the  $\beta$  configuration to this monoxime on the basis of its infrared spectrum in chloroform solution. He argued that since the bonded O - H stretching frequency and the carbonyl stretching frequency of the monoxime in the solid state remained unchanged in dilute chloroform solution, the hydrogen bonding must be intramolecular, i.e.,



He used  $\beta$  - benzil monoxime as a model.

For  $\beta$  - benzil monoxime the carbonyl stretching frequency ( $1675\text{ cm}^{-1}$ ) is the same in both solid and solution spectra. In the  $\alpha$  isomer the carbonyl vibration shifts from  $1645\text{ cm}^{-1}$  for the solid to  $1670\text{ cm}^{-1}$  for solutions. Based on the analogy with the benzil monoximes Sadler assigned the 2,2' - pyridilmonoxime m.p. 207°C the  $\beta$  configuration.

In his discussion Sadler only considered the possibility of hydrogen bonding between the oxime hydrogen and the carbonyl oxygen. He neglected to consider hydrogen bonding between the oxime hydrogen and the pyridine nitrogen, i.e.

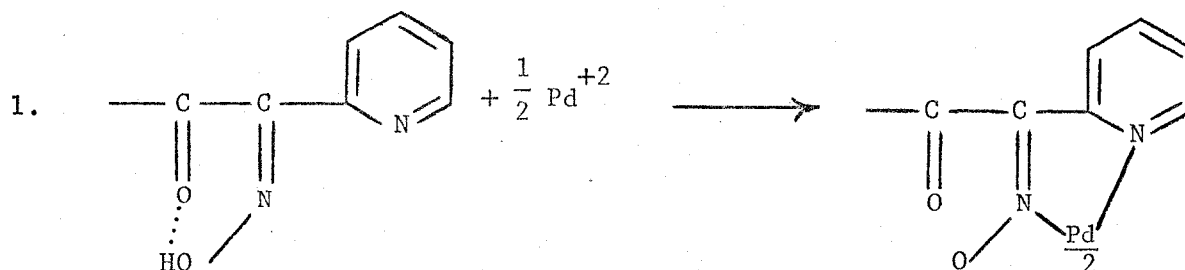


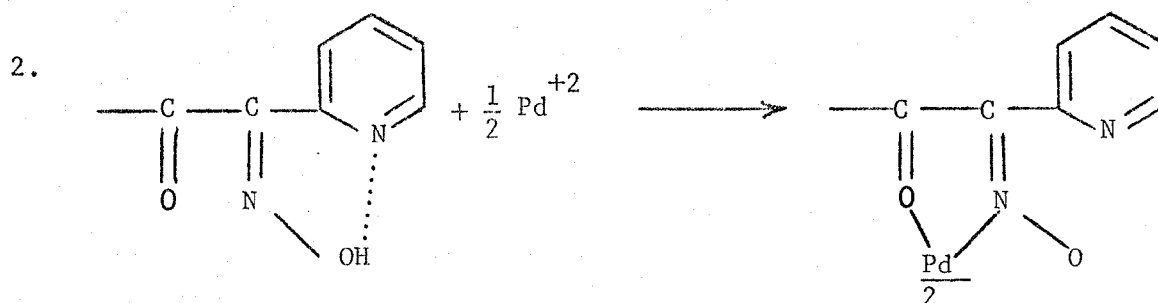
In this case the hydrogen bonding is also intramolecular and the carbonyl stretching frequency would not change in going from the solid state to a dilute solution. Thus Sadler's argument is equally valid for both isomers and hence cannot be used to distinguish between the two.

Dornow and Bruncken (26) reported the synthesis of a 2,2' - pyridil-monoxime m.p.  $198^{\circ}\text{C}$  by the nitrosation of desoxy -  $\alpha$  - pyridoin in 50% yield but assigned no configuration.

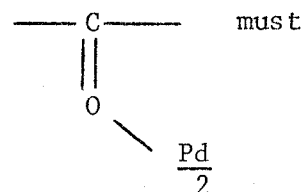
The monoxime prepared by our synthetic procedure had a m.p. of  $193 - 194^{\circ}\text{C}$ . The infrared spectrum did not differ significantly from that reported by Sadler. The infrared spectrum of a potassium bromide disc contained a strong carbonyl band at  $1695\text{ cm}^{-1}$  and a broad hydroxyl band at  $3060 - 3200\text{ cm}^{-1}$ . When the spectrum of a dilute chloroform solution was run, there was no shift in the carbonyl frequency.

The palladium and cobalt chelates had carbonyl stretching frequencies at  $1682\text{ cm}^{-1}$  and  $1660\text{ cm}^{-1}$  respectively. The hydroxyl band noted in the infrared spectrum of the monoxime was absent in the spectra of the chelates. The shift in the carbonyl band to lower frequencies indicates that something has happened to the carbonyl oxygen. There are only two possibilities:



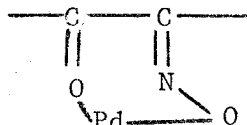


If 1 were true, then the carbonyl stretch would either remain unchanged or shifted to higher frequencies. The carbonyl vibration was shifted to lower frequencies, therefore 1 as a possibility is eliminated. This leaves only 2. Therefore we can state that

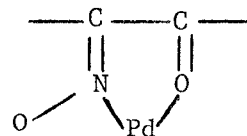


have taken place. This indicates that palladium is bonded to the carbonyl oxygen. The same argument would apply if the cobalt chelate was used as the example.

The only question remaining is whether the covalent bond is with the nitrogen or the oxygen of the oxime group. If bonding is through the oxygen we obtain:



This is an extremely distorted six membered ring. We have found that molecular models of the above structure are very difficult to make. If the bonding is through the oxime nitrogen, we obtain:



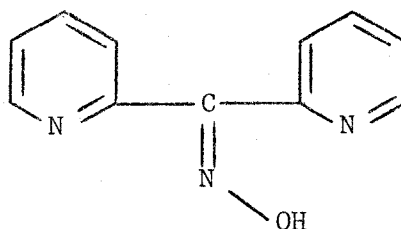
which is a stable five membered ring.

From the above evidence and arguments the 2,2' - pyridilmonoxime m.p. 193 - 194°C is assigned the  $\alpha$  configuration.

The infrared spectra did not yield information on the purity of the isomer. We used NMR data to prove that only one isomer was present.

Kleinspehn et. al. (27) showed that solutions of oximes in dimethyl sulfoxide exhibit a hydroxyl proton resonance signal whose chemical shift value is essentially concentration independent and thus characteristic of the particular oxime. Tanaka, Shona and Shinra (28) showed that the three dioxime isomers of benzil gave sharp signals for the hydroxyl proton and they also found that the chemical shifts were not affected by mixing of isomers and thus they were able to determine and identify mixtures of the three isomers. Other workers (29,30) also used NMR spectra to assess the purity and determine the structure of various oximes.

The chemical shift of the hydroxyl proton ( in 10% W/V deuterated dimethyl sulfoxide) of the monoxime isolated by our synthetic procedure was 11.78 ppm. relative to tetramethyl silane. The presence of only one band indicated the presence of only one isomer. Furthermore the chemical shift of the hydroxyl proton of 2,2' - dipyridyl ketoxime (VI) was 11.81 ppm.



(VI)

The electronic environment of the hydroxyl protons of 2,2' - pyridyl

ketoxime and the  $\alpha$  isomer are very similar and hence we would expect the chemical shifts to be the same. This is further evidence for the assignment of the  $\alpha$  configuration to the 2,2' - pyridilmonoxime m.p. 193-194°C.

### 3) Structure of the Palladium and Cobalt Chelates

From the isolated chelates it was found that the reagent to metal ratio was 2:1 for palladium and 3:1 for cobalt. A continuous variations plot also indicated a ligand to metal ratio of 2:1 for the palladium chelate (Table I and Fig. 2.). For both chelates the carbonyl shift to lower frequencies and the disappearance of the hydroxyl band on chelation indicates bonding through the carbonyl oxygen and the nitrogen of the oxime group. The formation of an extremely distorted six membered ring precludes bonding through the oxime oxygen. The two chelates may be represented by the following structures:

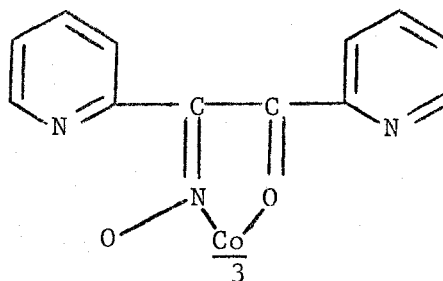
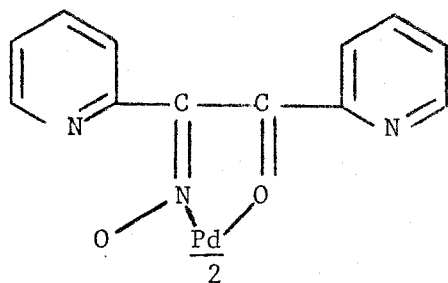


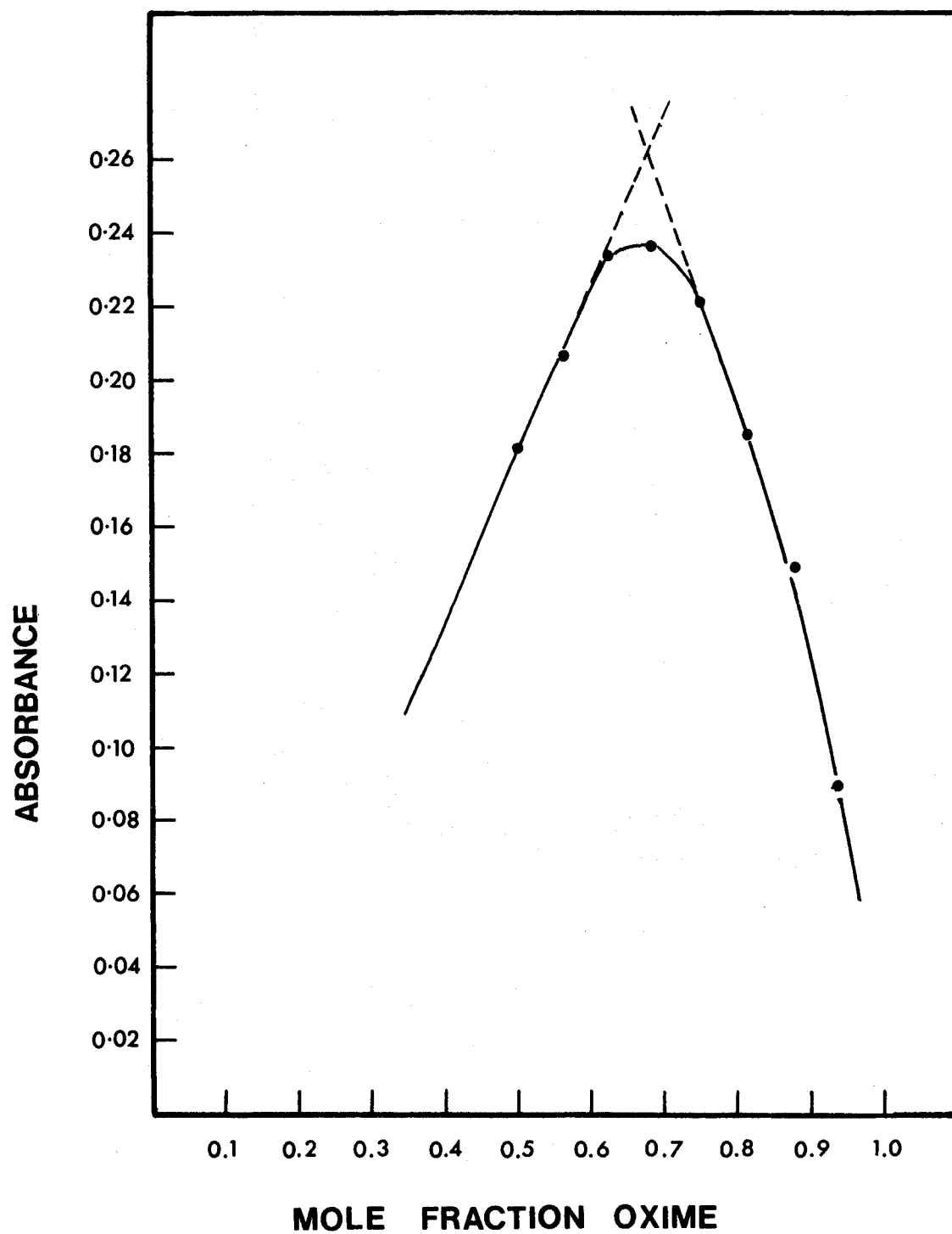


TABLE I  
CONTINUOUS VARIATIONS DATA FOR PALLADIUM (II)  
AND 2,2' - PYRIDILMONOXIME

Sample	Mole Fraction Oxime	Absorbance
1	0.936	0.089
2	0.878	0.149
3	0.814	0.185
4	0.750	0.221
5	0.685	0.236
6	0.625	0.233
7	0.564	0.206
8	0.500	0.181
9	0.438	0.143
10	0.374	0.104
11	0.312	0.097
12	0.250	0.076
13	0.188	0.054

Figure 2. Continuous variations plot for the palladium  
(II) 2,2' - pyridilmonoxime complex.

FIGURE 2



#### 4) Reactions of Metals with 2,2' - Pyridilmonoxime

The metals and parameters studies are summarized in Table II. The visible spectra of the various complexes are presented in Fig.3 and Fig.4. Of the metals studied only palladium and cobalt possessed properties suitable for their analytical determination. The other metals studied were extremely pH dependent in their reactions and drastic changes in both the visible spectra and extinction coefficients occurred with a change in pH. For the nickel complex no reproducible spectra could be obtained. For the iron system the maximum is at 540 nm at pH 2 and 578 nm at pH 11. Manganese gave only a weak colour reaction and hence was not investigated further.

A continuous variations plot (Table III and Fig. 5) for the copper system indicated the formation of a 2:1 complex. A continuous variations plot for the iron system (Table IV and Fig. 6) indicated the formation of at least two complexes.

The cobalt, palladium, iron and nickel chelates are readily extractable into chloroform. The gold chelate is extractable into chloroform in the presence of a large excess of perchlorate ions.

#### D. SUMMARY AND CONCLUSIONS

The synthesis and properties of 2,2' - pyridilmonoxime have been described. On the basis of spectroscopic evidence the 2,2' - pyridilmonoxime m.p. 193 - 194<sup>o</sup>C was assigned the  $\alpha$  configuration. The study of the reactions of various metals with the reagent indicated that it could be applied to the determination of trace amounts of palladium and cobalt. The palladium and cobalt chelates were isolated and analyzed. From the infrared data it was postulated that bonding to the metal occurs

TABLE II  
REACTIONS OF METALS WITH 2,2' - PYRIDILMONOXIME

Metal Ion	Optimum pH Range	$\lambda_{\text{max}}(\text{nm})$	Molar Absorptivity
Pd (II)	0.5 - 2	416	$1.1 \times 10^4$
Co (III)	4.5 - 7	408	$1.7 \times 10^4$
Au (III)	0.8 - 1.5	434	$1.5 \times 10^4$
Cu (II)	7 - 9	424	$4.5 \times 10^3$
Fe (III)	8 - 9	574	$1.1 \times 10^4$
Ni (II)	Slight Reaction		
Mn (II)	Slight Reaction		

Figure 3. Spectral absorption curves of metal 2,2' - pyridilmonoxime complexes.

1. Au (III) complex in aqueous solution.
2. Cu (II) complex in aqueous solution.
3. Pd (II) complex in chloroform solution.
4. Co (III) complex in chloroform solution.
5. Ni (II) complex in aqueous solution.

FIGURE 3

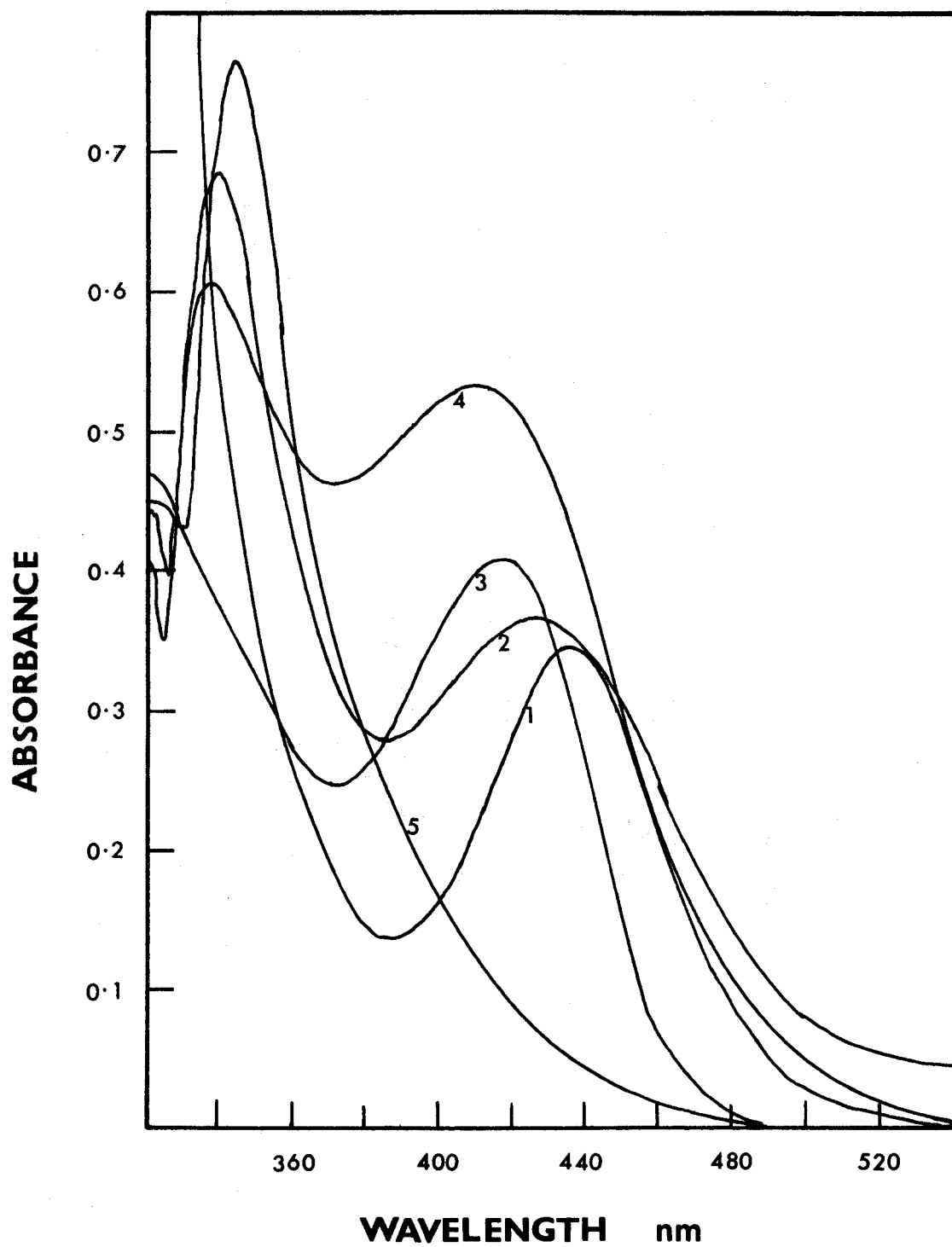
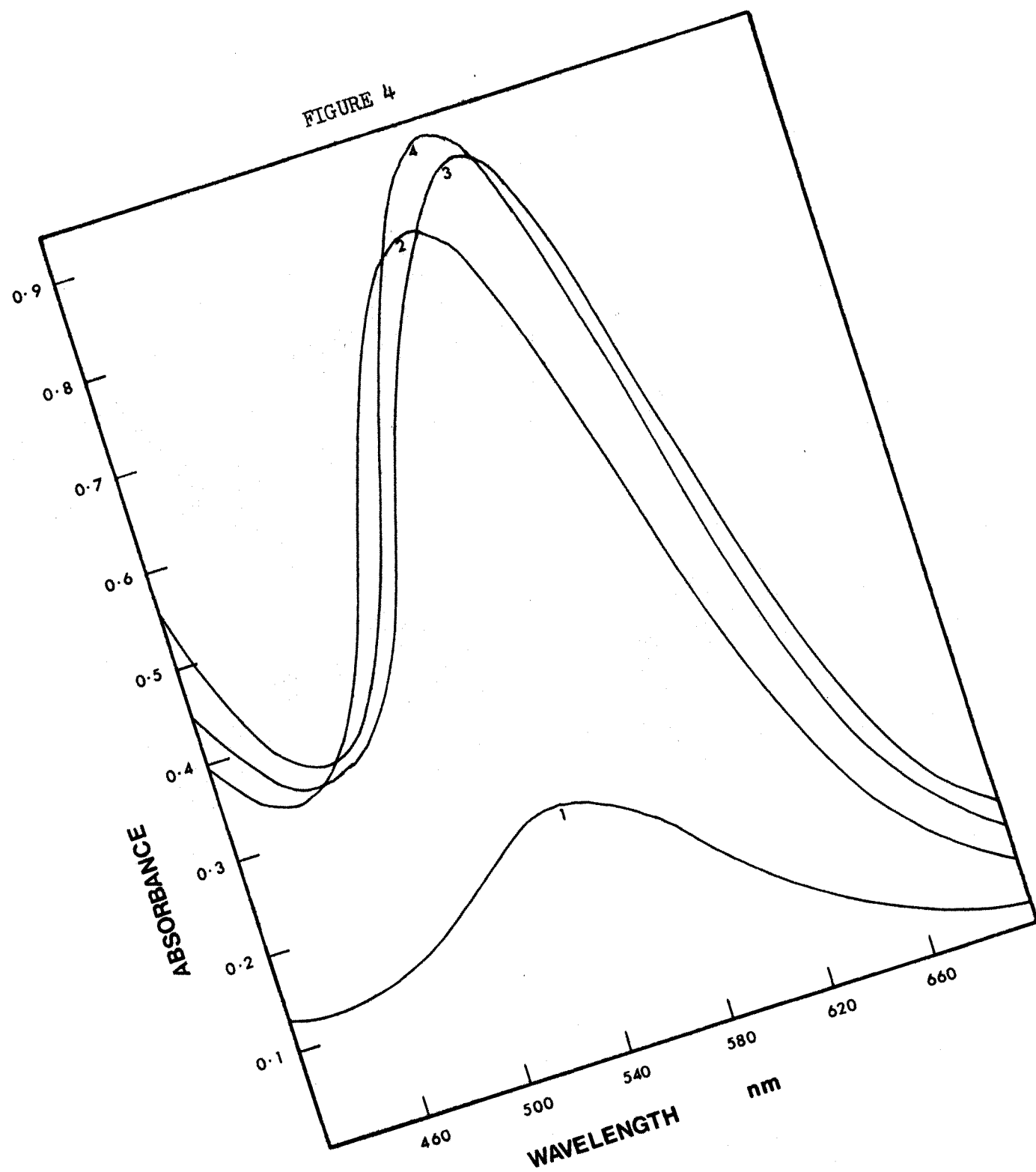


Figure 4. Spectral absorption curves of the iron (III)

2,2' - pyridilmonoxime complex at varying pH.

1. pH = 2
2. pH = 4
3. pH = 11
4. pH = 7





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TABLE III  
CONTINUOUS VARIATIONS DATA FOR COPPER (II)  
AND 2,2' - PYRIDILMONOXIME

Sample	Mole Fraction Oxime	Absorbance
1	0.938	0.146
2	0.875	0.263
3	0.813	0.354
4	0.750	0.383
5	0.688	0.384
6	0.625	0.377
7	0.563	0.344
8	0.500	0.355
9	0.438	0.319
10	0.375	0.264
11	0.313	0.218
12	0.250	0.166
13	0.188	0.127
14	0.125	0.078
15	0.063	0.048

Figure 5. Continuous variations plot for the copper  
(II) 2,2' - pyridilmonoxime complex.

FIGURE 5

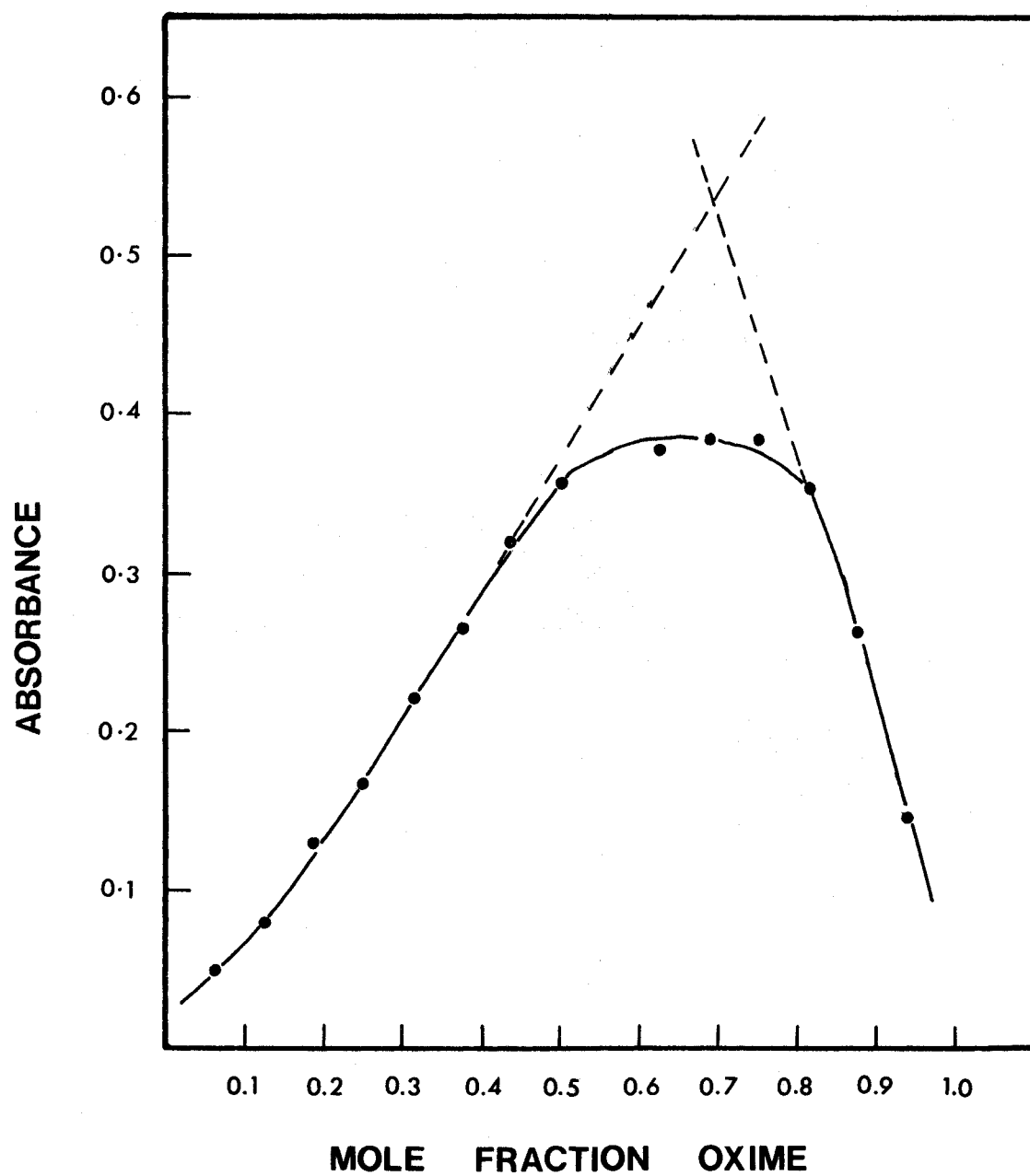
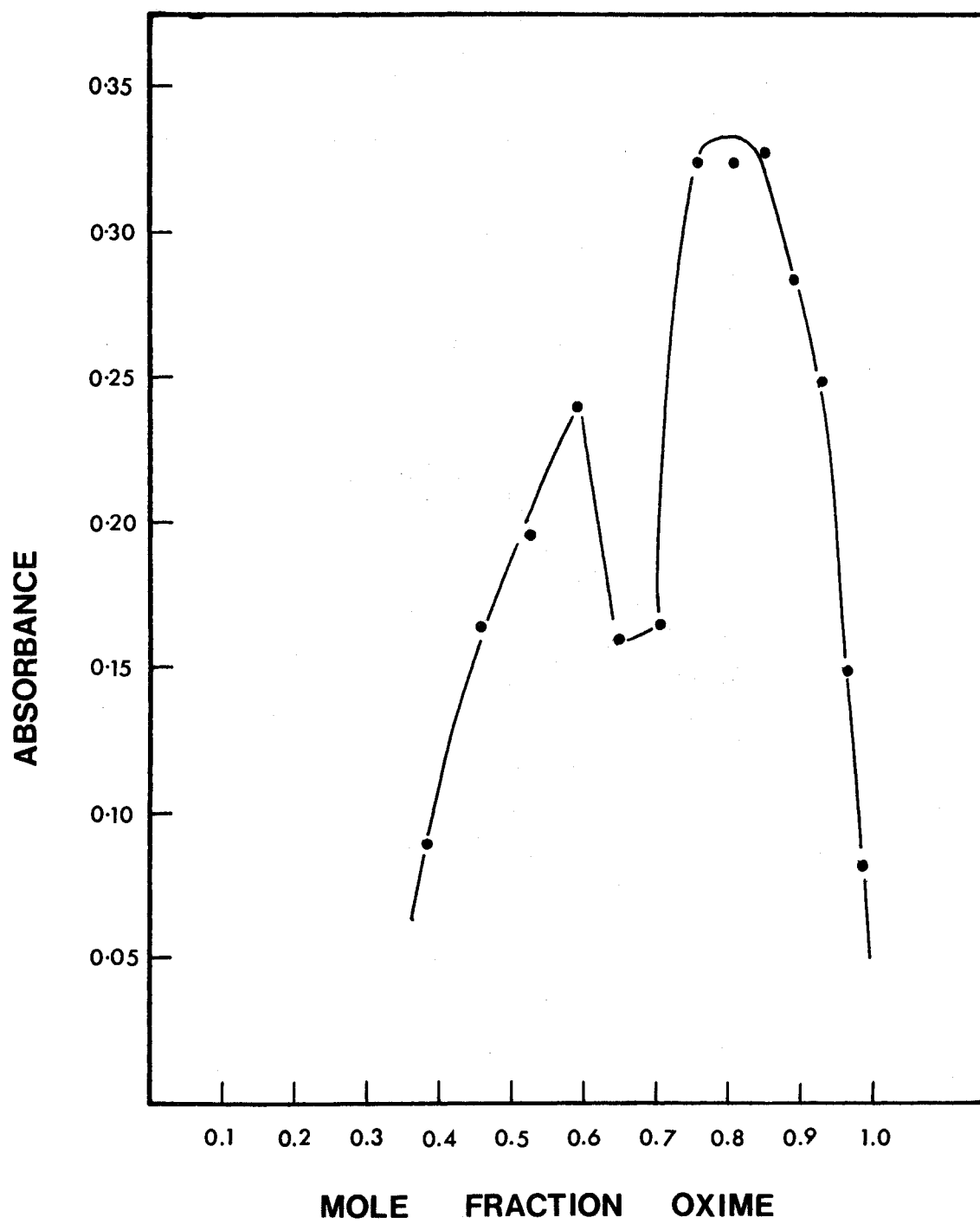


TABLE IV  
CONTINUOUS VARIATIONS DATA FOR IRON (III)  
AND 2,2' - PYRIDILMONOXIME

Sample	Mole Fraction Oxime	Absorbance
1	0.992	0.042
2	0.983	0.095
3	0.965	0.149
4	0.928	0.248
5	0.889	0.283
6	0.848	0.327
7	0.803	0.322
8	0.755	0.323
9	0.704	0.165
10	0.650	0.158
11	0.590	0.244
12	0.527	0.196
13	0.457	0.164
14	0.382	0.090

Figure 6. Continuous variations plot for the iron  
(III) 2,2' - pyridilmonoxime system.

FIGURE 6



through the carbonyl oxygen and the oxime nitrogen.



## CHAPTER III

### SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

#### WITH 2,2' - PYRIDILMONOXIME

##### A. INTRODUCTION

Many reagents, both inorganic and organic, have been used for the spectrophotometric determination of palladium. Critical evaluations of the various reagents and methods have been published by Beamish and McBryde (31,32) and Beamish (33). The list of reagents and methods has been kept up to date by the reviews of Boltz and Mellon (34 -37).

The inorganic reagents used include tin (II) salts. For the range 0.5 - 2.5 ppm of palladium, tin (II) salts provide useful spectrophotometric procedures. The use of tin (II) salts has been studied by Ayres and Meyer (38), Ayres and Alsop (39), and Pantini and Piccardi (40). Palladium has also been determined spectrophotometrically as the bromide (41) and as the thiocyanate (42).

Most of the organic reagents used for the spectrophotometric determination of palladium fall into four broad categories: nitrosoamines, nitrosonaphthols, mercapto compounds and oximes.

Of the nitrosoamines, p - nitrosodiphenylamine, p - nitrosodimethylaniline and p - nitrosodiethylaniline have been recommended by Overholser and Yoe (43). This class of reagents produces extremely sensitive reactions with palladium; however, the effectiveness of the methods is reduced since the pH must be strictly controlled, the colour intensity is very sensitive to the presence of salts and there are many

interferences.

Both 1 - nitroso - 2 - naphthol (44) and 2 - nitroso - 1 - naphthol (45) have been used for the determination of palladium in the range 0.5 - 5 ppm. Of the various nitrosonaphthols used for the determination of palladium, 1 - nitroso - 2 - naphthol - 3,6 - disulphonate (Nitroso - R Salt) is considered to be the best (46).

Representative examples of mercapto compounds used as reagents for palladium include: 2 - mercapto - 4,5 - dimethylthiazole (47), 2 - mercaptobenzimidazole (48), 2 - mercaptoquinoline (49), and dithio - oxamide (50) and its derivatives.

Oximes have received much attention as reagents for palladium since they are the only reagents for palladium which approach specificity. Dimethylglyoxime has been used for the spectrophotometric determination of palladium by Kodama (51).  $\alpha$ - Furfuraldioxime was used by Menis and Rains (52) to produce a yellow complex which, in an aqueous ethanol medium, obeyed Beer's Law at 420 nm. Nioxime (53) and its derivatives (54) have also been used as reagents for palladium.

Some of the more recent reagents for palladium are arsenazo III (55), 2,2' - dipyridylglyoxime (56), dimethylsulfonazo III (57), and pyridine - 2 - carboxaldehyde - 2' - pyridyl hydrazone (58). The most sensitive method to date is based upon ternary complex formation with 1, 10 - phenanthroline or pyridine and Rose Bengal Extra (59). The molar absorptivities are  $5 \times 10^4$  (aqueous) and  $1.25 \times 10^5$  (organic) in the presence of a 1000 - fold molar excess of EDTA as mass masking agent.

In the present work, 2,2' - pyridilmonoxime was investigated as a new reagent for the spectrophotometric determination of palladium. The reaction between palladium (II) and 2,2' - pyridilmonoxime was investigated to determine such factors as optimum concentration of reagent, influence of pH on complex formation and extraction, choice of solvent, effect of diverse ions and precision and accuracy. A procedure was developed for the spectrophotometric determination of palladium (II).

## B. EXPERIMENTAL

### 1) Instruments

The absorbance measurements were made with a Hitachi Perkin - Elmer Model 139 spectrophotometer, a Beckman DB spectrophotometer equipped with a Sargent Model SRL recorder and 1.00-cm. silica cells. A Sargent Model LS pH meter was used for pH measurements.

### 2) Reagents

2,2' - Pyridilmonoxime solution: A 1% W/V solution in 0.6 M hydrochloric acid was prepared. This solution was stable for five days.

Palladium (II) solution: A stock solution of palladium was prepared by dissolving anhydrous palladium (II) chloride (Fisher Scientific) in concentrated hydrochloric acid, diluting to one litre with distilled water and standardizing with 2,2' - dipyridyl ketoxime (21).

Diverse cation solutions: prepared from reagent grade chloride or nitrate salts.

Diverse anion solutions: prepared from reagent grade sodium or potassium salts.

Chloroform: A.C.S. grade was used.

### 3) Recommended Procedure

Transfer an aliquot of sample solution containing 50 - 200 ug of palladium (II) to a 100-ml beaker. To the beaker add 4 ml of freshly prepared reagent solution and adjust the pH to 1 by the addition of a few drops of dilute potassium hydroxide or hydrochloric acid solution. Allow the colour to develop for 15 minutes and extract with three 5-ml portions of chloroform. Filter the extracts through a funnel containing a small plug of glass wool into a 25-ml glass - stoppered graduated cylinder. Wash with a few ml of chloroform. Make up to volume with chloroform and measure the absorbance at 416 nm against a reagent blank prepared in a similar manner. Calculate the amount of palladium from a previously prepared calibration curve.

### C. RESULTS

#### 1) Effect of pH

The optimum pH range for chelate formation and extraction was 0.5 to 2.0 (Table V). At pH values greater than 4 the spectral characteristics of the chelate change.

#### 2) Absorption Spectra

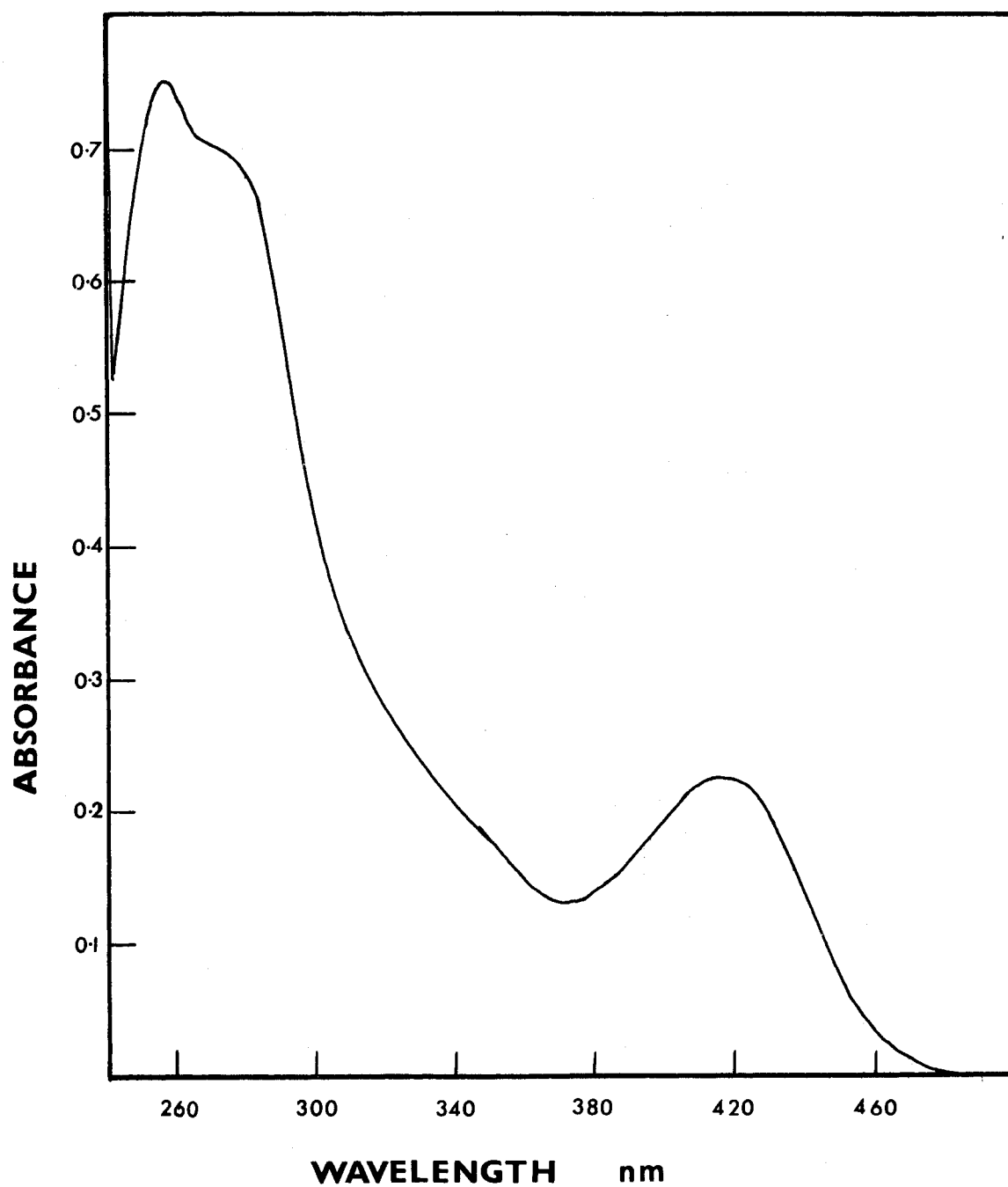
The absorption spectra of the pure palladium chelate and the reagent blank are presented in Fig. 7. The palladium chelate has absorption maxima at 416 and 256 nm and a shoulder at 272 nm. The 416 nm maximum was chosen for analytical use since the reagent does not absorb at this wavelength.

TABLE V  
INFLUENCE OF pH ON COMPLEX FORMATION  
AND EXTRACTION (4.0 ppm Pd)

pH	Absorbance of Organic Extract
0.0	0.405
0.5	0.410
1.0	0.413
1.5	0.410
2.0	0.411
2.5	0.405
3.2	0.390
4.0	0.345

Figure 7. Absorption spectrum of the pure palladium  
chelate in chloroform.

FIGURE 7



### 3) Effect of Reagent Concentration

It was found that at least a 20 - fold excess of reagent is required for satisfactory results.

### 4) Effect of Time

Chelate formation was complete in 10 minutes. The chloroform extracts were stable for at least 24 hours when kept in the dark.

### 5) Effect of Solvents

Using the recommended procedure the chelate was completely extracted into chloroform, methylene chloride and ethylene dichloride and partially extracted into carbon tetrachloride, benzene and amyl alcohol.

### 6) Beer's Law

A straight line was obtained over the range 1 - 13 ppm when absorbance was plotted against concentration (Table VI and Fig. 8.).

### 7) Optimum Concentration Range and Sensitivity of the Method

The optimum concentration range evaluated by Ringbom's method was 2 - 8 ppm (Table VII and Fig. 9). The molar absorptivity of the chelate at 416 nm was  $1.1 \times 10^4$  and the Sandell sensitivity was 0.01  $\mu\text{g cm}^{-2}$ .

### 8) Precision and Accuracy

The precision and accuracy of the method was studied by analyzing solutions containing known amounts of palladium. The results are summarized in Table VIII.



TABLE VI  
BEER'S LAW DATA FOR THE SPECTROPHOTOMETRIC  
DETERMINATION OF PALLADIUM WITH 2,2' - PYRIDILMONOXIME

Sample	Palladium Concentration ppm	Absorbance
1	1.00	0.095
2	2.00	0.198
3	3.00	0.307
4	4.00	0.410
5	5.00	0.511
6	6.00	0.619
7	7.00	0.714
8	8.00	0.820
9	9.00	0.919
10	10.00	1.032
11	12.00	1.236
12	13.00	1.332
13	14.00	1.438

Figure 8. Beer's Law plot for the determination of palladium with 2,2' - pyridilmonoxime.

FIGURE 8

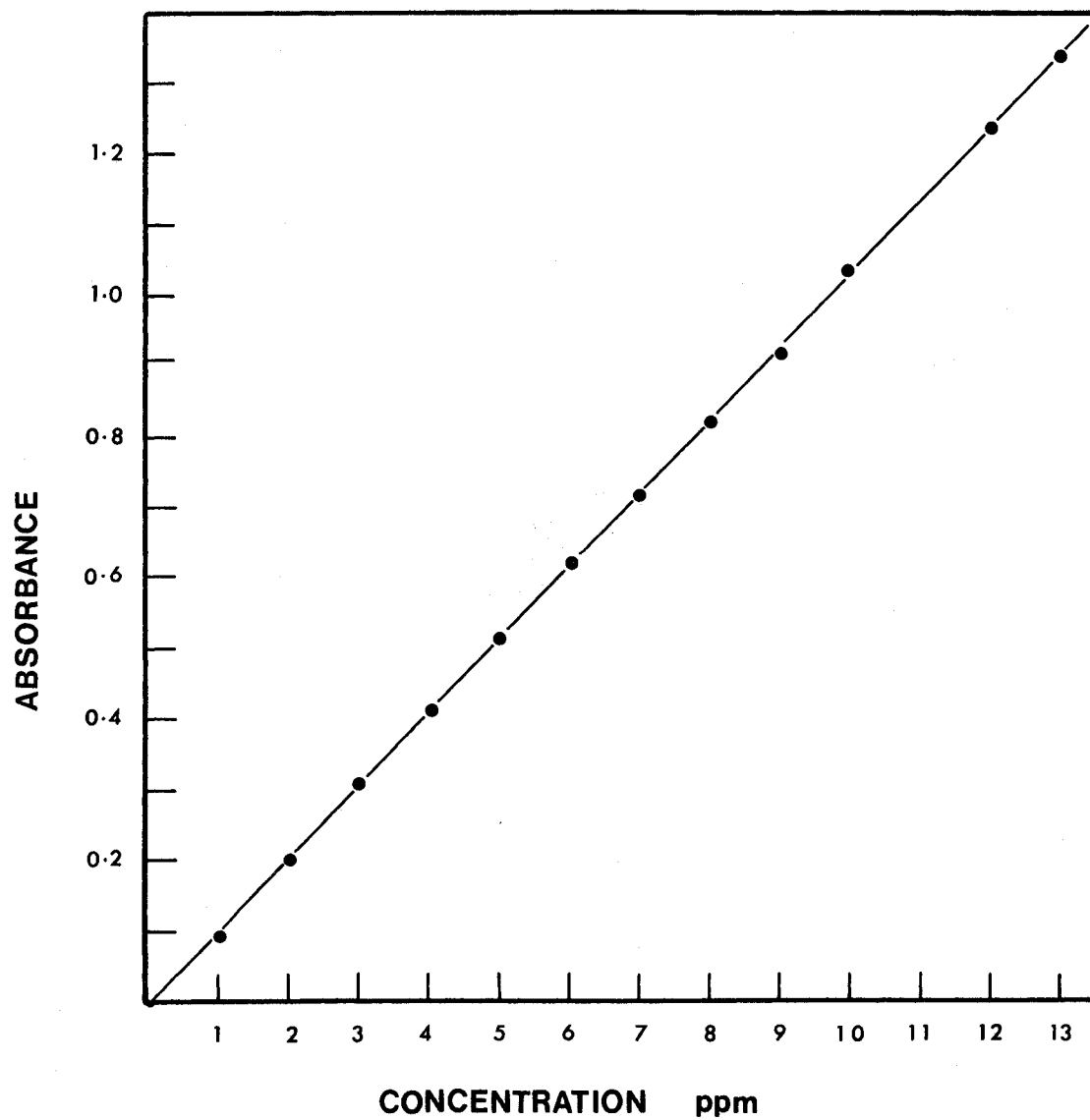


TABLE VII  
RINGBOM DATA FOR THE DETERMINATION  
OF PALLADIUM WITH 2,2' - PYRIDILMONOXIME

Concentration ppm	Log c	Absorptancy 100 -% T
1.00	0.000	19.5
2.00	0.301	36.5
3.00	0.477	51.8
4.00	0.602	61.1
5.00	0.699	69.2
6.00	0.778	76.0
7.00	0.845	80.7
8.00	0.903	84.9
9.00	0.954	88.0
10.00	1.00	90.7
12.00	1.079	94.2
13.00	1.114	95.4
14.00	1.146	96.3

Figure 9. Ringbom plot for the determination of palladium with 2,2' - pyridilmonoxime.

FIGURE 9

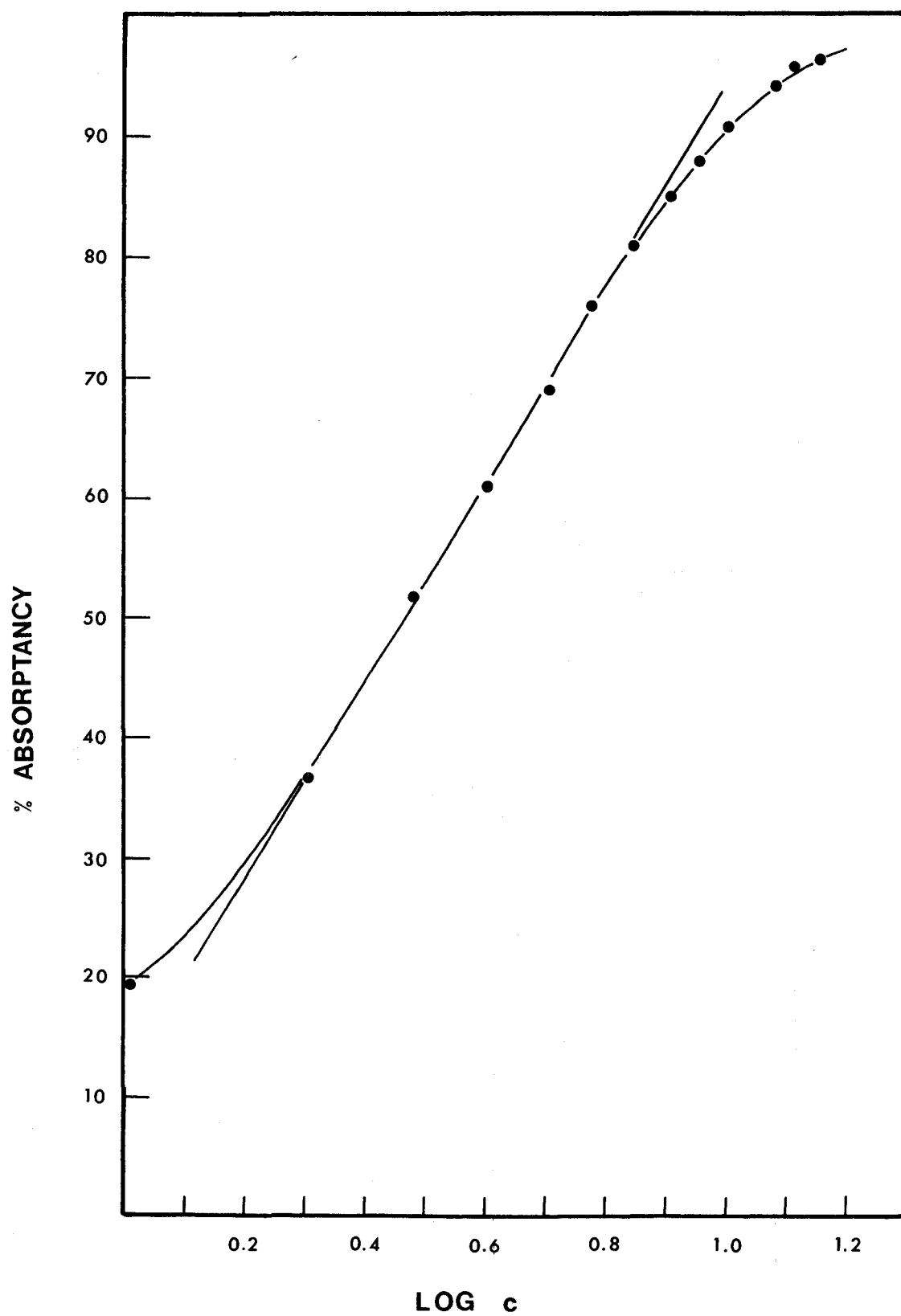


TABLE VIII  
PRECISION AND ACCURACY

Palladium Taken, ppm	*Palladium Found, ppm	Relative Error, %	Standard Deviation, ppm	Range, ppm
2.00	2.00	0.00	0.05	0.14
4.00	4.00	0.00	0.03	0.10
8.00	7.99	0.13	0.04	0.12

\* Each result is the average of ten separate analyses.

### 9) Effect of Diverse Ions

Five mg of diverse ion were added to a 100-ml beaker containing 100 ug of palladium and the recommended procedure was followed. The following ions did not interfere:  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Tl}^+$ ,  $\text{Be}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Mn}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Pt}^{+2}$ ,  $\text{Hg}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{UO}_2^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Cr}^{+3}$ ,  $\text{Ga}^{+3}$ ,  $\text{As}^{+3}$ ,  $\text{Rh}^{+3}$ ,  $\text{In}^{+3}$ ,  $\text{Bi}^{+3}$ ,  $\text{Ce}^{+3}$ ,  $\text{Ti}^{+4}$ ,  $\text{Zr}^{+4}$ ,  $\text{Hf}^{+4}$ ,  $\text{Pt}^{+4}$ ,  $\text{Th}^{+4}$ ,  $\text{Se}^{+4}$ ,  $\text{Te}^{+4}$ ,  $\text{V}^{+5}$ ,  $\text{Re}^{+7}$ ,  $\text{Os}^{+8}$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{-2}$ , EDTA and citrate. The following ions did not interfere when used in conjunction with the appropriate masking agents: 5 mg of  $\text{Cu}^{+2}$  masked with 5 ml of 0.1 M EDTA; 5 mg  $\text{Fe}^{+3}$  masked with 15 mg  $\text{F}^-$ ; 5 mg  $\text{Co}^{+2}$  masked with 10 mg  $\text{F}^-$ ; 1 mg  $\text{WO}_4^{-2}$  masked with 10 mg  $\text{F}^-$ . The system could also tolerate 500 ug  $\text{Ru}^{+2}$ , 250 ug  $\text{Ir}^{+2}$ , 250 ug  $\text{Ir}^{+3}$ , 500 ug  $\text{Ag}^+$  and 100 ug of  $\text{Au}^{+3}$ . Cyanide ion interfered severely and must be absent.

### D. DISCUSSION

In the present work, a procedure was developed for the spectrophotometric determination of divalent palladium based on the formation of an intensely coloured 2:1 complex with 2,2' - pyridilmonoxime. This complex was extracted into chloroform resulting in a procedure which was free from interferences. The method was rapid, and the coloured complex was stable. Beer's Law was obeyed and there were no critical parameters to contend with.

There are many spectrophotometric methods for palladium that are more sensitive than the one described in this dissertation (60); however, they require careful adjustment of parameters and they are not very selective. The major advantage of the present system is its



selectivity. Another advantage of the system is that it is carried out under acidic conditions where there is no danger of the formation of hydroxides and hydrated oxides. These two features should make the method ideal for the analysis of trace amounts of palladium in ores, alloys and other substances.

#### E. SUMMARY AND CONCLUSIONS

The spectrophotometric determination of palladium described in this dissertation involved the extraction of the palladium - 2,2' - pyridilmonoxime complex from an aqueous solution of pH 0.5 - 2.0 into chloroform and subsequent measurement of the organic extract at 416 nm.

A 1% W/V solution of 2,2' - pyridilmonoxime in 0.6 M hydrochloric acid was used as the reagent solution.

Various parameters were investigated. The maximum yellow colour intensity developed between a pH of 0.5 and 2.0. A large excess of reagent was used and no absorption due to reagent occurred at 416 nm. Chelate formation was complete in 10 minutes and the chloroform extracts were stable for at least 24 hours when kept in the dark. The method obeyed Beer's Law over a wide concentration range and proved to be both precise and accurate. Furthermore, an extensive foreign ion study indicated that the procedure is widely applicable and most metals commonly associated with palladium do not interfere.

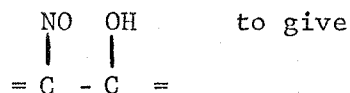
The procedure for the spectrophotometric determination of palladium with 2,2' - pyridilmonoxime has been previously published (19).

CHAPTER IV  
SPECTROPHOTOMETRIC DETERMINATION OF COBALT  
WITH 2,2' - PYRIDILMONOXIME

A. INTRODUCTION

Various spectrophotometric methods have been developed for the determination of microgram quantities of cobalt. They have been described and evaluated by Sandell (61), Snell (62), Charlot (63) and Williams (64). In their reviews of light absorption spectrometry Boltz and Mellon (34 - 37) listed the new reagents proposed for the spectrophotometric determination of cobalt.

Some of the most sensitive methods for cobalt are based on its reaction with compounds containing the group



strongly coloured chelates. It is generally accepted that reagents of this type form complexes with trivalent cobalt, the reagent also serving as oxidizing agent. A peculiarity of all the reagents with this grouping is that they react quantitatively with cobalt in weakly acidic or neutral solution but, once formed, the chelate is not appreciably dissociated by strong acids. The two main reagents belonging to this class are 1 - nitroso - 2 naphthol and sodium 1 - nitroso - 2 - hydroxynaphthelene - 3,6 - disulphonate (nitroso - R salt).

The nitroso - R salt method (65) is extremely sensitive and has found wide application in the determination of microgram amounts of cobalt in both biological (66, 67) and inorganic matrices (68 - 70). Methods involving the use of 1 - nitroso - 2 naphthol (71,72) are less

sensitive than those employing the nitroso - R salt; however, 1 - nitroso - 2 - naphthol forms a neutral chelate with cobalt which can be extracted into an organic solvent and hence greater amounts of iron, nickel and copper can be tolerated.

Some of the recent reagents proposed for the spectrophotometric determination of cobalt include benzil mono - (2 - pyridyl) hydrazone (73), succinimide (74) and 4 - (2 - triazolylazo) resorcinol (75).

In the present work, 2,2' - pyridilmonoxime was proposed as a new spectrophotometric reagent for the determination of microgram quantities of cobalt. The reagent reacted with cobalt to form an intensely coloured water-soluble chelate which was easily extractable into chloroform.

Studies were undertaken to determine such factors as optimum concentration of reagent, effect of time, influence of pH on complex formation and extraction, choice of solvent, effect of diverse ions and precision and accuracy. A procedure was developed for the spectrophotometric determination of cobalt.

## B. EXPERIMENTAL

### 1) Instruments

A Hitachi Perkin - Elmer Model - 139 spectrophotometer, a Beckman DB spectrophotometer equipped with a Sargent Model - SRL recorder and 1.00-cm silica cells were used for the spectrophotometric measurements. A Sargent Model - LS pH meter was used for pH measurements.

## 2) Reagents

Standard cobalt solution: A stock solution was prepared by dissolving ultra - pure cobalt metal (Research Inorganic Chemical Corp., Sun Valley, California) in aqua regia, evaporating to near dryness and diluting to 1 liter with doubly distilled water. This was further diluted to give a standard cobalt solution of 8.86 ug / ml.

Reagent solution: A 1% W/V solution in 95% ethanol was used. This solution was stable for at least one month. Diverse cation solutions: Reagent grade chloride or nitrate salts were used. Arsenic, molybdenum, rhenium and selenium solutions were prepared from the corresponding oxides.

Diverse anion solutions: These were prepared from reagent grade sodium or potassium salts. Chloroform: ACS grade was used.

## 3) Recommended Procedure

Take an aliquot of sample containing 9 -90 ug of cobalt and place it in a 100-ml beaker. Add 5 ml of reagent solution and adjust the pH to 5 by the addition of a few drops of dilute hydrochloric acid or potassium hydroxide solution. Allow the colour to develop for 5 minutes and transfer the solution to a 60-ml separatory funnel. Extract the chelate with three 5-ml portions of chloroform. The funnel stem contained a plug of glass wool to remove traces of water. The extracts were added to 25-ml glass-stoppered graduated cylinders. Make up to volume with chloroform and measure the absorbance at 408 nm against a reagent blank prepared in a similar manner. The amount of cobalt is determined from a previously prepared calibration curve.

## C. RESULTS

### 1) Effect of pH

The optimum pH range for chelate formation and extraction was 4.5 - 7.0 (Table IX).

### 2) Absorption Spectra

The absorption spectra of the pure cobalt chelate and the reagent blank are presented in Fig. 10. The cobalt chelate has absorption maxima at 408, 300 and 268 nm. There was slight absorption due to reagent at 408 nm and all analytical measurements were made at this wavelength. The molar absorptivity at 408 nm was  $1.7 \times 10^4$ .

### 3) Effect of Reagent Concentration

A large excess of reagent was required for satisfactory results. Five ml of reagent solution were sufficient over the concentration range 9 - 90 ug of cobalt.

### 4) Effect of Time

Chelate formation was complete in 5 minutes. The chloroform extracts were stable for at least 2 days.

### 5) Effect of Solvents

Using the recommended procedure the chelate was completely extracted into chloroform, methylene chloride and ethylene dichloride and partially extracted into benzene, ethyl acetate, amyl alcohol and carbon tetrachloride.

### 6) Conformity to Beer's Law

A Beer's Law plot at the absorption maximum of 408 nm was found to be linear over the range 0.4 - 4.0 ppm as illustrated from the data in Table X and Fig. 11.

TABLE IX  
EFFECT OF pH ON CHELATE FORMATION  
AND EXTRACTION (1.77 ppm Cobalt)

pH	Absorance Of Organic Extract
1.5	0.446
2.0	0.485
3.0	0.510
4.0	0.512
4.5	0.530
5.0	0.525
6.0	0.525
7.0	0.530
8.0	0.502
10.0	0.485
11.0	0.475

Figure 10. Absorption spectrum of the pure cobalt  
chelate in chloroform.

FIGURE 10

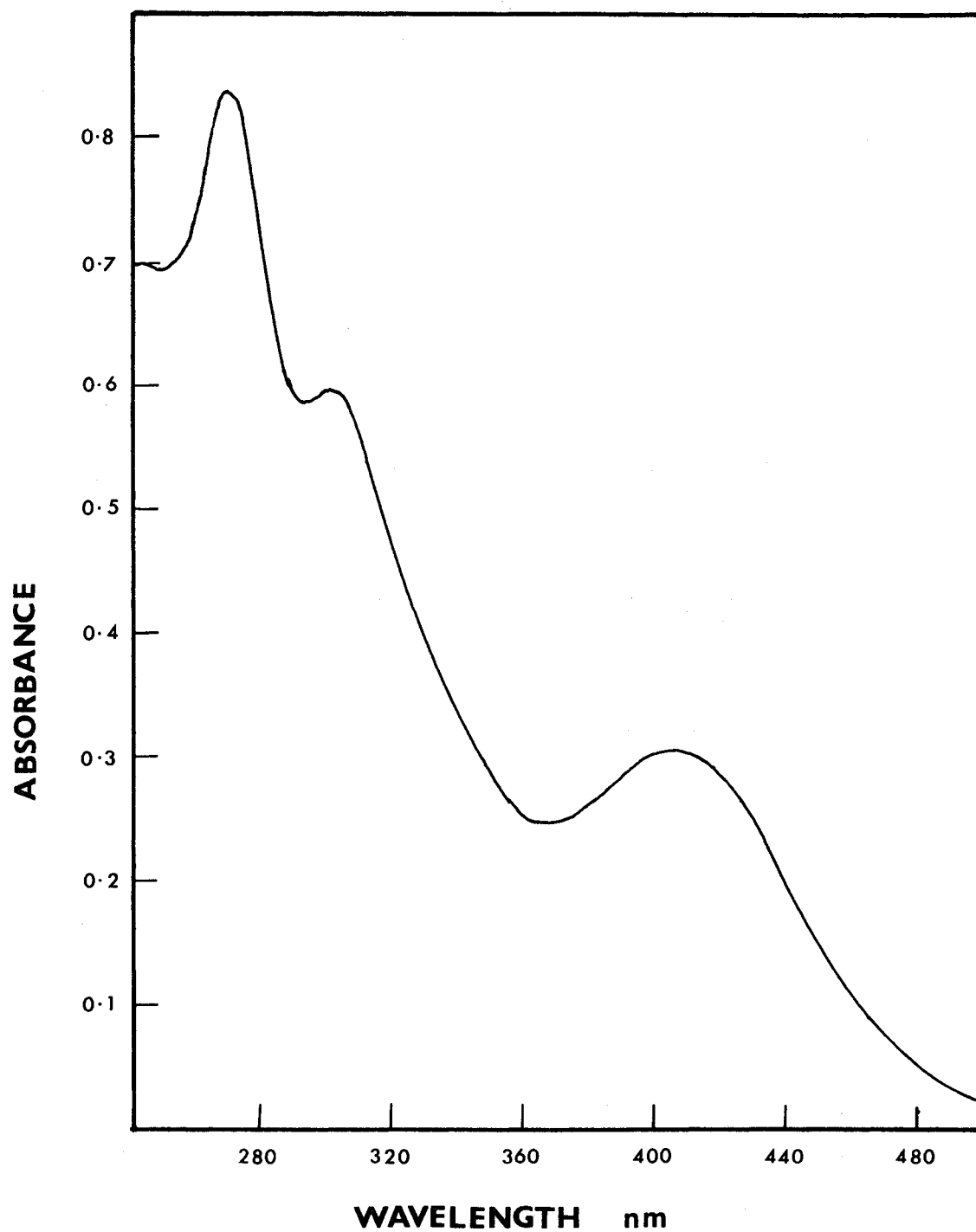


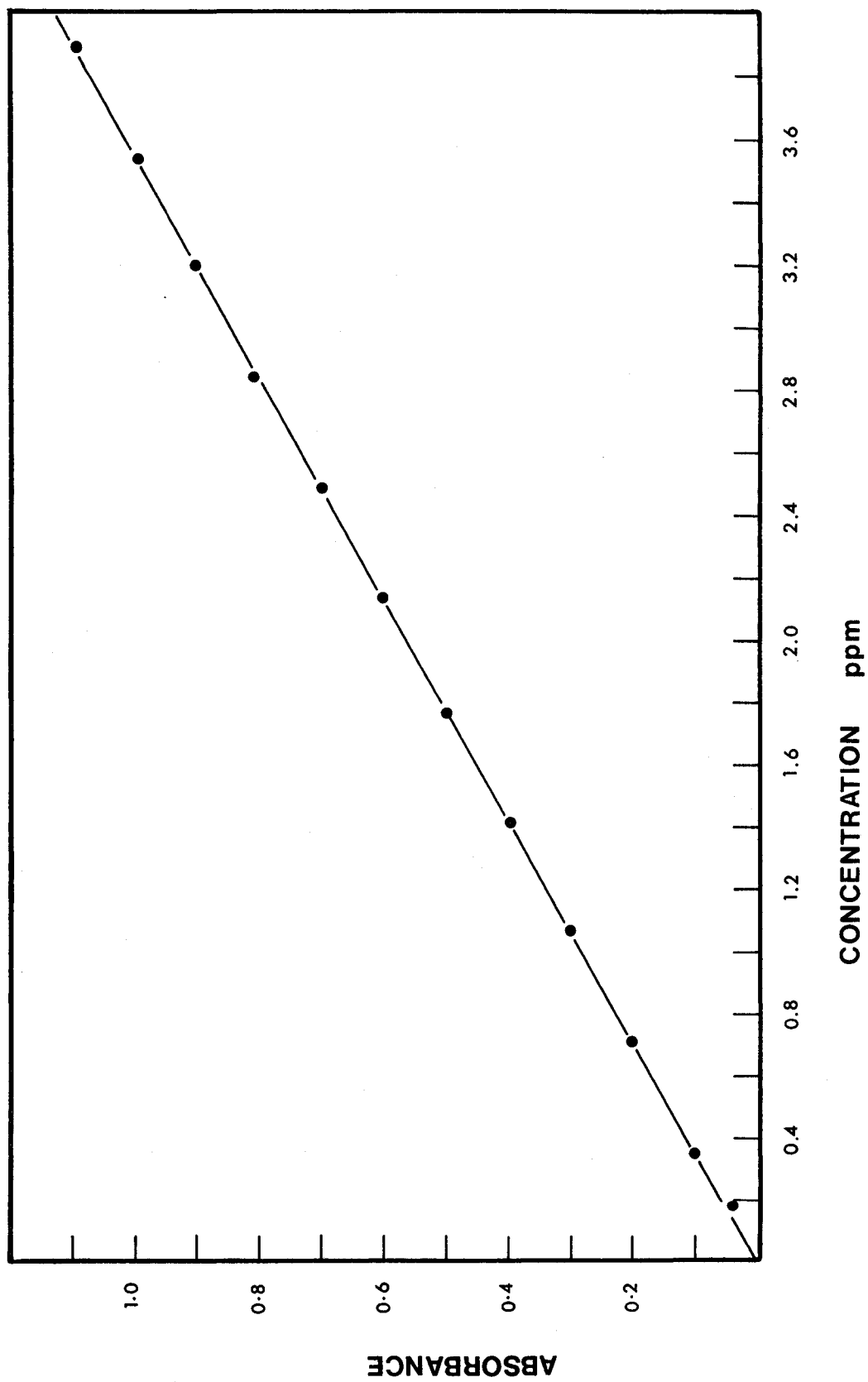


TABLE X  
BEER'S LAW DATA FOR THE SPECTROPHOTOMETRIC  
DETERMINATION OF COBALT WITH 2,2' - PYRIDILMONOXIME

Sample	Cobalt Concentration ppm	Absorbance
1	0.18	0.041
2	0.35	0.098
3	0.71	0.199
4	1.06	0.300
5	1.42	0.399
6	1.77	0.502
7	2.13	0.604
8	2.48	0.698
9	2.84	0.809
10	3.19	0.902
11	3.54	0.998
12	3.90	1.098
13	4.25	1.204

Figure 11. Beer's Law plot for the determination of cobalt with 2,2' - pyridilmonoxime.

FIGURE 11



### 7) Optimum Concentration Range and Sensitivity of the Method

The optimum concentration range evaluated by Ringbom's method was 0.7 - 2.8 ppm (Table XI and Fig. 12). The molar absorptivity at 408 nm was  $1.7 \times 10^4$  and the Sandell sensitivity was .0035  $\mu\text{g cm}^{-2}$ .

### 8) Precision and Accuracy

The precision and accuracy of the method was studied by analyzing solutions containing known amounts of cobalt. The results are summarized in Table XII.

### 9) Effect of Diverse Ions

Five mg of a diverse ion were added to a 100-ml beaker containing 44.3  $\mu\text{g}$  of cobalt and the recommended general procedure was followed. An error of 2% in the absorbance reading was considered tolerable. The following ions did not interfere:  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Hg}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Tl}^+$ ,  $\text{Pb}^{+2}$ ,  $\text{Se}^{+4}$ ,  $\text{Bi}^{+3}$ ,  $\text{Re}^{+7}$ ,  $\text{Ce}^{+3}$ ,  $\text{Ga}^{+3}$ ,  $\text{Nb}^{+5}$ ,  $\text{ZrO}^{+2}$ . Two mg of  $\text{Sn}^{+4}$ ,  $\text{Al}^{+3}$ ,  $\text{Th}^{+4}$  and  $\text{Ba}^{+2}$  could be tolerated. A tolerance limit of 1 mg was found for the following ions:  $\text{Cd}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Te}^{+4}$ ,  $\text{Ti}^{+4}$ ,  $\text{Hf}^{+4}$ ,  $\text{Zr}^{+4}$  and  $\text{VO}_3^-$ . Five mg of  $\text{Fe}^{+3}$  were masked with 5 ml of 10% sodium pyrophosphate and 1 mg of  $\text{Mn}^{+2}$  was masked with 2 ml of 10% sodium pyrophosphate. The system could also tolerate 500  $\mu\text{g}$   $\text{Ag}^+$ ,  $\text{As}^{+3}$ ,  $\text{Sb}^{+3}$ ,  $\text{In}^{+3}$  and 100  $\mu\text{g}$  of  $\text{Rh}^{+3}$ ,  $\text{Ir}^{+3}$ ,  $\text{Mo}^{+6}$  and  $\text{Be}^{+2}$ . The interferences due to  $\text{Cu}^+$ ,  $\text{Cu}^{+2}$  and  $\text{Au}^{+3}$  were eliminated by prior extractions with dithizone. At a pH of 2, 1 mg of each of the ions was quantitatively extracted by three 20-ml portions of  $10^{-3}$  M dithizone in chloroform. One mg of nickel was masked with 3 ml of 10% sodium citrate. One mg of  $\text{CN}^-$  did

TABLE XI  
RINGBOM DATA FOR THE DETERMINATION OF  
COBALT WITH 2,2' - PYRIDILMONOXIME

Concentration ppm	Log c	Absorptancy 100 - % T
0.18	-0.745	8.9
0.35	-0.456	20.0
0.71	-0.149	36.8
1.06	0.025	49.8
1.42	0.152	60.1
1.77	0.248	68.4
2.13	0.328	75.2
2.48	0.395	80.0
2.84	0.453	84.5
3.19	0.504	87.5
3.54	0.549	89.9
3.90	0.591	92.0
4.25	0.628	93.8

Figure 12. Ringbom plot for the determination of cobalt with 2,2' - pyridilmonoxime.

FIGURE 12

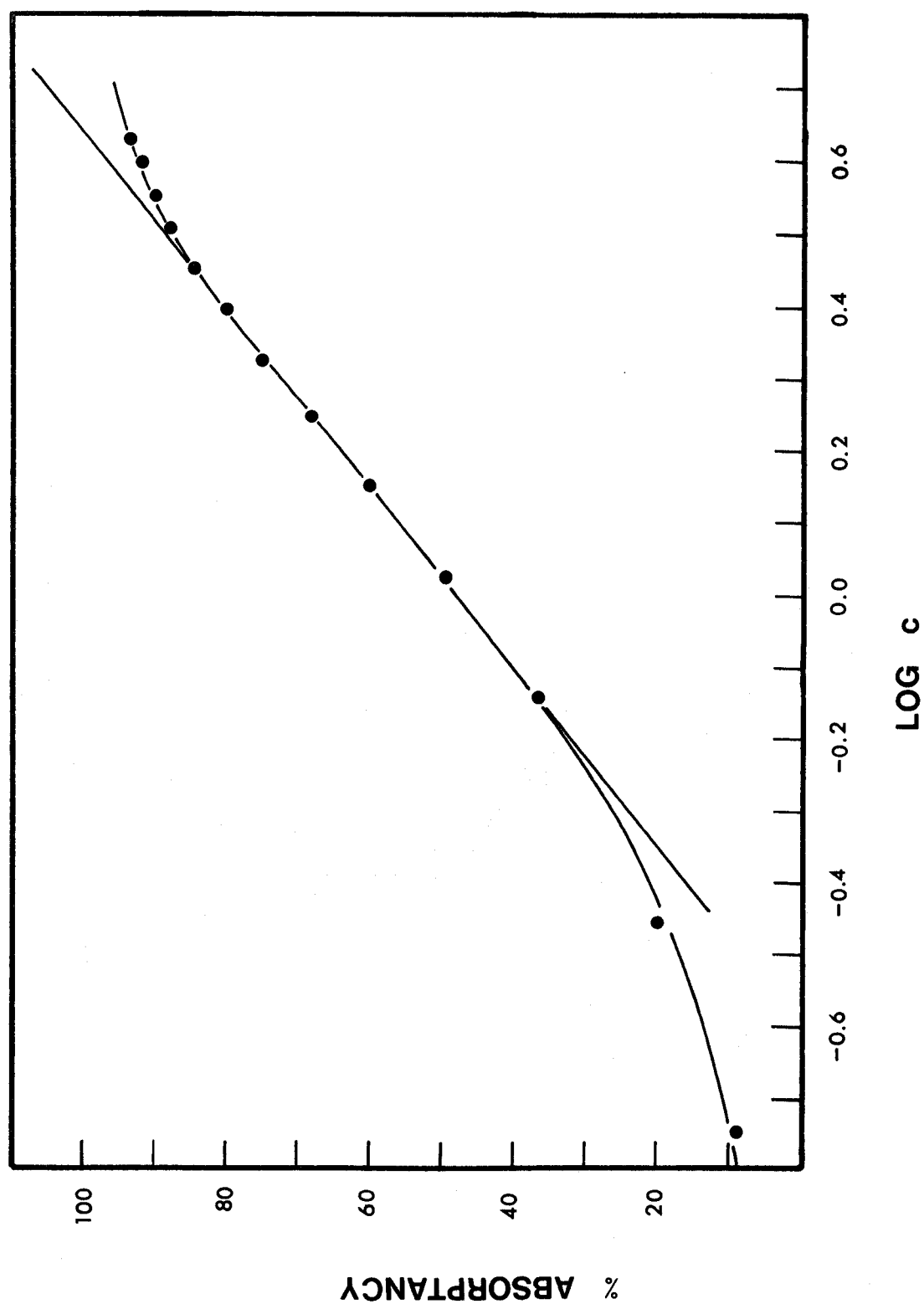


TABLE XII  
PRECISION AND ACCURACY

Cobalt Taken, ppm	Cobalt * Found, ppm	Relative Error, %	Standard Deviation, ppm	Range, ppm
0.71	0.72	+1.40	0.01	0.01
1.42	1.42	0.00	0.01	0.03
2.84	2.84	0.00	0.02	0.04

\* Each result is the average of eight separate analyses.



not destroy the cobalt chelate and this fact was used to eliminate the interference due to  $\text{Pd}^{+2}$  and  $\text{Pt}^{+2}$ . After the cobalt chelate was developed, 1 mg of  $\text{CN}^-$  was added. This destroyed the palladium and platinum complexes. The cobalt chelate was then extracted. The following ions interfered:  $\text{Sn}^{+2}$ ,  $\text{Cr}^{+3}$ ,  $\text{Ru}^{+3}$ , EDTA and large amounts of  $\text{CN}^-$ .

#### D. DISCUSSION

In the present work, 2,2' - pyridilmonoxime has been applied to the spectrophotometric determination of cobalt. The procedure has the advantages of sensitivity, simplicity, rapidity and a tolerance to many foreign ions. The use of masking agents and prior solvent extraction to remove interferences has greatly increased the selectivity of the method. The metals commonly associated with cobalt either do not interfere or can be easily masked or separated.

Analysis of the cobalt chelate indicated that the cobalt was in the trivalent state. The cobalt was probably oxidized to the trivalent state by dissolved oxygen. Furthermore, that cobalt exists in the trivalent state is supported by the stability of the chelate in strong acid solutions, a characteristic of  $d^6$  spin-paired complexes (76).

#### E. SUMMARY AND CONCLUSIONS

The spectrophotometric determination of cobalt involved the extraction of 9 - 90 ug of cobalt as a 3:1 chelate with 2,2' - pyridilmonoxime. The chloroform extraction was performed from an aqueous solution of pH 4.5 - 7.0. The absorbance of the chloroform extract was measured at 408 nm, the wavelength of maximum absorption of the

complex and at this wavelength there was negligible absorption due to the excess reagent. The amount of cobalt was calculated from a previously prepared calibration curve.

Various parameters such as influence of pH on complex formation and extraction, effect of reagent, effect of time, choice of solvent, applicability of Beer's Law and foreign ions were studied. The optimum concentration range was 0.7 - 2.8 ppm. Determination of known amounts of cobalt showed the procedure to be both accurate and precise. An extensive foreign ion study showed the procedure to be widely applicable.

The procedure for the spectrophotometric determination of cobalt with 2,2' - pyridilmonoxime has been previously published (20).

## CHAPTER V

### SUMMARY AND CONCLUSIONS

The reagent 2,2' - pyridilmonoxime has been synthesized and characterized. On the basis of spectral evidence it has been assigned the  $\alpha$  configuration. The reagent was found to be very specific and sensitive for palladium and cobalt and procedures were developed for the determination of these two metals.

The various parameters studied included the following: effect of pH, effect of reagent concentration, effect of time, effect of diverse ions, applicability of Beer's Law and the effect of solvents.

Because of the sensitivity and specificity of the two procedures developed for palladium and cobalt, they should find wide applicability in the analysis of a wide variety of materials.

PART II

THE ANALYTICAL APPLICATIONS OF

2,2' - DIQUINOLYL KETOXIME

## CHAPTER I

### INTRODUCTION

Organic reagents, no matter what the type, show more or less selectivity, but rarely true specificity. The selectivity of chelate-forming reagents varies with the reactive group in the molecule. Most organic reagents with a given reactive group in the molecule will form complexes of similar properties with a number of elements, particularly those closely related in chemical properties. A few organic reagents show a unique behaviour by reacting (in the limiting case) with only one element.

In choosing an analytical method for trace analysis, sensitivity and specificity are the two most important characteristics to consider. Increasing the sensitivity of a particular reagent is best achieved by increasing the number of chromophores. The realization that the selective action of many organic compounds can be ascribed to the presence of particular atomic groupings introduces the possibility of "tailoring" such molecules to increase their utility in chemical analysis. For example, the introduction of various groups can prevent the reaction with some metals and not with others and hence make the reagent more specific. The development of "tailor-made" organic reagents is readily seen in the analogues of 1,10 - phenanthroline.

One of the most important class of organic reagents contains the atomic grouping -  $N = C - C = N -$  . Chromogens containing this atomic grouping are commonly referred to as ferroin reagents. This class of

reagents forms complexes with ions of the transition metals and with  $\text{Cu}^+$ ,  $\text{Zn}^{+2}$  and  $\text{Cd}^{+2}$ . 1,10 - Phenanthroline is perhaps the best known ferroin reagent.

The effect of substituents in the aromatic ring systems of 1,10 - phenanthroline have been studied intensively with a view of increasing the sensitivity and selectivity. In the phenanthroline complexes of Fe(II) and Cu(I), it was found that: (a) almost any substituent, including  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ , Cl, and  $\text{NO}_2$ , will raise the molar absorbance; (b) the effect of the substituents  $\text{CH}_3$  and  $\text{C}_6\text{H}_5$  is much greater in the 4 and 7 positions than elsewhere in the ring; (c) substitution in the 2 and 9 positions makes the ferrous complexes unstable and hence makes the reagents specific for Cu(I); (d) phenyl groups raise the absorbance more than methyl groups (77 - 80). Thus by adding particular substituents to the phenanthroline nucleus, it was possible to improve the sensitivity and selectivity. Similar relationships were found with 2,2' - bipyridines (81) and 2,2' - biquinolines (82). On the basis of these relationships extremely sensitive and selective reagents have been developed for iron (83) and copper (84).

Pyridine oximes are another group of important ferroin reagents. The applications of pyridine oximes to the analysis of trace amounts of transition metals are numerous. Phenyl -  $\alpha$  - pyridyl ketoxime has been used for the spectrophotometric determination of palladium (85) and gold (86). Quinoline - 2 - aldoxime has been used for the spectrophotometric determination of Cu(I) (87). The reagent 2,2' - dipyridyl

ketoxime has been applied to the spectrophotometric determination of gold (88, 89), palladium (90), cobalt (91) and iron (92).

Methyl substitution in the 6 position of the pyridine ring renders the particular oxime more specific for Cu(I). This fact has been used to synthesize a new spectrophotometric reagent for Cu(I) (93).

In the present work, the reactions of metals with 2,2' - diquinolyl ketoxime (an analogue of 2,2' - dipyridyl ketoxime) were investigated with a view of applying the reagent to the spectrophotometric determination of various metals. It was hoped that the expansion of the pyridine nucleus into a quinoline nucleus would increase the sensitivity and selectivity. The reagent formed analytically useful complexes with cobalt and palladium and spectrophotometric methods were developed for these two metals.

## CHAPTER II

### SYNTHESIS AND PROPERTIES OF 2,2' - DIQUINOLYL

#### KETOXIME AND ITS REACTION WITH METALS

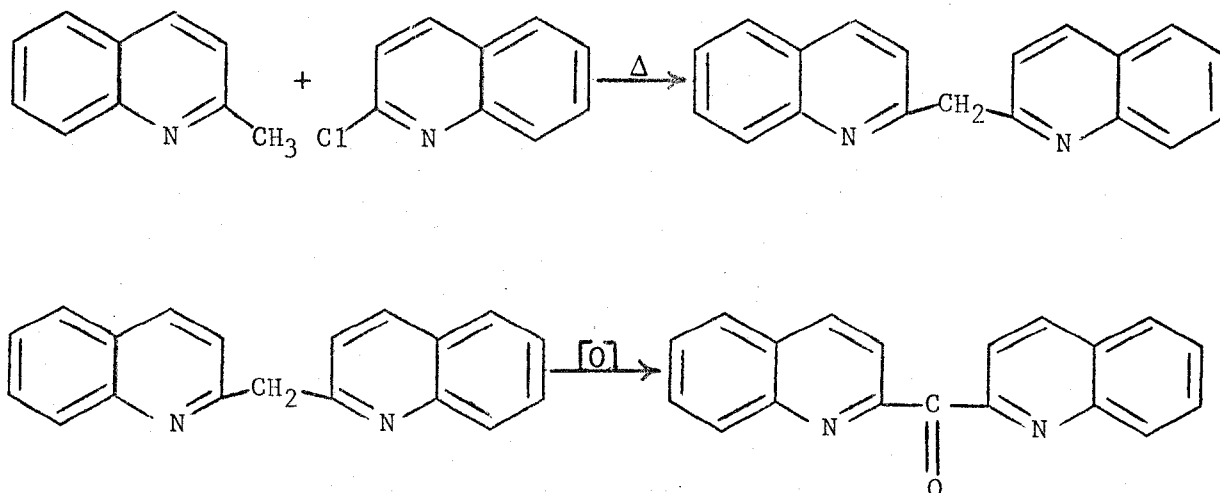
##### A. INTRODUCTION

The present study involved the synthesis of a new ferroin reagent and its application to the analysis of trace amounts of cobalt and palladium. The reagent was synthesized by the reaction of 2,2' - diquinolylketone with hydroxylamine hydrochloride and its properties were studied. The reactions of metals with 2,2' - diquinolyl ketoxime were investigated with a view of applying the reagent to the analysis of trace amounts of metals. The reagent was found to be highly selective and sensitive for palladium and cobalt.

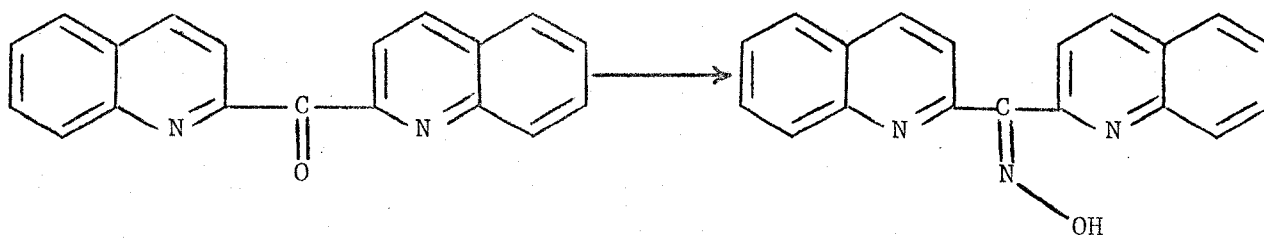
##### B. EXPERIMENTAL

###### 1) Synthesis of 2,2' - Diquinolyl Ketoxime

The synthetic route is summarized by the following series of reactions:







2,2' - Methylenequinoline was prepared using modifications in the procedure described by Scheibe (94). To 28.6 g (0.2 mole) of 2 - methyl - quinoline in a 500-ml round bottom flask equipped with a reflux condenser and thermometer was added 16.4 g (0.1 mole) of 2 - chloroquinoline. The resulting solution was slowly and evenly heated with a microburner. At approximately 245<sup>o</sup> C the solution began to boil and at around 260<sup>o</sup>C a vigorous exothermic reaction took place with a rise in temperature to about 290<sup>o</sup>C. The mixture was cooled and to the resulting dark red paste was added a solution of 6 g of potassium hydroxide in 250 ml of ethanol. After heating on a steam bath, the precipitate of potassium chloride was filtered and the alcohol removed using a rotary evaporator. The residual red viscous oil was slowly added to 3500 ml of boiling petroleum ether (30 - 60<sup>o</sup>C boiling range). On evaporation to approximately 500 ml there was obtained 18.5 g of crude product which on recrystallization from petroleum ether gave 13.5 g of orange-red crystals, m.p. 101 - 103<sup>o</sup>C. Analysis calculated for C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>: C, 84.42%; H, 5.22%; N, 10.36%. Found: C, 84.37%; H, 5.24%; N, 10.36%.

The 2,2' - methylenequinoline was oxidized to 2,2' - diquinolyketone using the procedure of Hamana and Yamazaki (95).

To 5.0 g of 2,2' - diquinolyketone dissolved in 200 ml of hot

ethanol was added a solution of 5 g of hydroxylamine hydrochloride and 8 g of potassium hydroxide in 100 ml of water. The mixture was heated with stirring for 10 minutes, cooled and neutralized by dropwise addition of 3M hydrochloric acid. The resulting oxime was filtered and recrystallized from 500 ml of benzene. The yield was 5.0 g of fine white crystals, m.p. 207 - 208°C. Analysis calculated for  $C_{19}H_{13}N_3O$ : C, 76.24%; H, 4.38%; N, 14.04%. Found: C, 76.08%; H, 4.31%; N, 14.04%. Carbon, hydrogen and nitrogen analyses were done by Midwest Microlab Inc., Indianapolis, Indiana.

## 2) Apparatus

Nuclear Magnetic Resonance spectra were obtained, using 5% W/V solutions in deuterated dimethylsulfoxide with TMS as the internal standard, on a JNM - C - 60 HL spectrometer. Infrared spectra were obtained with a Beckman IR-12 using 1% potassium bromide discs. Ultra-violet spectra were obtained with a Beckman DB spectrophotometer equipped with a Sargent SRL recorder. Melting points were obtained with a Fisher - Johns Melting Point Apparatus. A Sargent Model - DR pH meter was used for pH measurements.

## 3) Chemicals

2 - Chloroquinoline and 2 - methylquinoline were obtained from Aldrich Chemical Company. Hydroxylamine Hydrochloride, analytical reagent grade from Mallinckrodt Chemical Works. Chloroform, benzene, pet ether and ethanol, A.C.S. grades were used.

#### 4) Reagent Solution

A 0.10% W/V solution in 95% ethanol was used.

#### 5) Standard Solutions

A stock solution of palladium was prepared by dissolving ultra-pure palladium wire (Alfa Inorganics, Beverly, Massachusetts) in aqua regia and diluting to volume with distilled water. A stock solution of copper was prepared by dissolving ultra-pure copper metal (Research Inorganic Chemical Corp., Sun Valley, California) in 1:1 nitric acid, evaporating to a small volume, adding 20 ml of 1:1 hydrochloric acid and diluting to volume with distilled water. A stock solution of gold was prepared by dissolving  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (Fisher Scientific) in distilled water and standardizing with hydroquinone (22). A stock solution of iron was prepared by dissolving pure iron wire (Fisher Scientific) in 1:1 hydrochloric acid and diluting to volume with distilled water. A stock solution of nickel was prepared by dissolving pure nickel powder in 1:1 nitric acid and diluting to volume with distilled water. A stock solution of cobalt was prepared by dissolving ultra-pure cobalt metal (Research Inorganic Chemical Corp., Sun Valley, California) in aqua regia, evaporating to near dryness and diluting to volume with distilled water.

Standard solutions of all of the metals were prepared by appropriate dilutions of the stock solutions.

#### 6) Procedure For the Study of the Reactions of Metals with 2,2' - Diquinolyl Ketoxime

An aliquot of the metal ion was transferred to a 50-ml beaker. To the acidified solution was added 1 ml of reagent solution. The pH

was adjusted with dilute potassium hydroxide or hydrochloric acid. The complex was allowed to develop for 10 minutes and then extracted into chloroform or benzene. The organic extracts were diluted to 25.0 ml in glass-stoppered graduated cylinders and the spectra recorded.

### C. RESULTS AND DISCUSSION

#### 1) Properties of 2,2' - Diquinolyl Ketoxime

The oxime is soluble in benzene, chloroform, methylene chloride, dimethylsulfoxide and dilute acids. It is insoluble in water and only very slightly soluble in ethanol.

The ultraviolet spectrum of 2,2' - diquinolyl ketoxime (in 95% ethanol) is shown in Fig. 13. The oxime has maxima at 280, 243 and 205 nm with molar absorptivities of  $1.2 \times 10^4$ ,  $4.9 \times 10^4$  and  $5.1 \times 10^4$  respectively.

In the infrared the oxime exhibits strong absorption at the following frequencies (in  $\text{cm}^{-1}$ ): 3140, 3010, 2850, 1612, 1593, 1558, 1499, 1421, 1292, 1119, 1029, 1013, 998, 934, 835, 812, 758, 623, 585 and 475.

The chemical shift of the oxime proton in a 5% W/V solution in deuterated dimethylsulfoxide was 12.12 ppm relative to TMS.

#### 2) Reactions of Metals with 2,2' - Diquinolyl Ketoxime

The metals and parameters studied are summarized in Table XIII. The visible spectra of the various complexes are presented in Fig. 14 and Fig. 15.

The reagent reacted with Ni(II) over the pH range 5 - 13.5.

Figure 13. Absorption spectrum of 2,2' - diquinolyl  
ketoxime in ethanol.

FIGURE 13

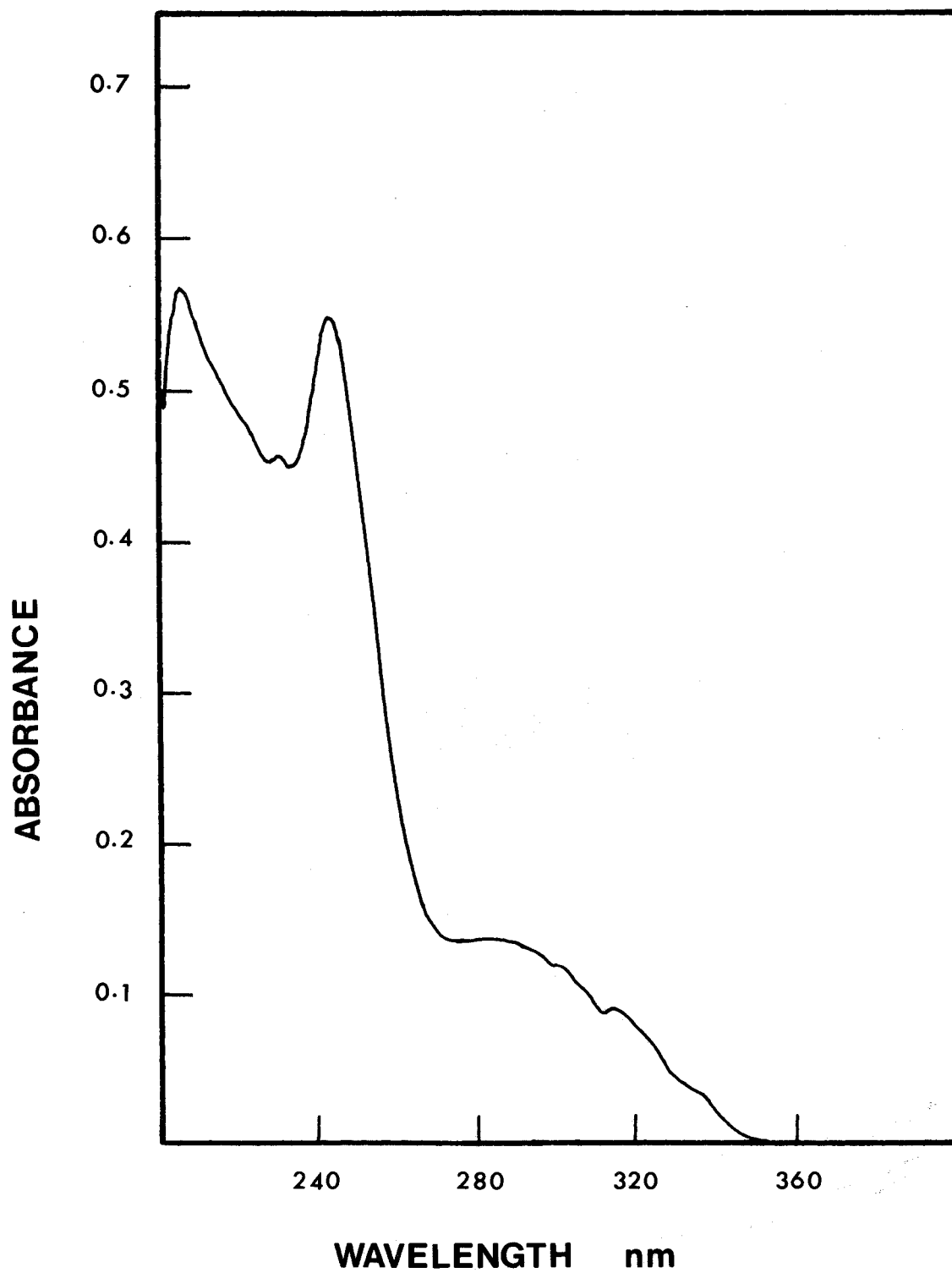


TABLE XIII  
REACTIONS OF METALS WITH 2,2' - DIQUINOLYL KETOXIME

Metal Ion	pH Range	$\lambda_{\max}$	Molar Absorptivity
Cobalt	13.8 - 2M KOH	365	$5.3 \times 10^4$
Pd (II)	6 - 13.5	478	$1.3 \times 10^4$
Ni (II)	9.5 - 12.5	374	$1.15 \times 10^4$
Cu (II)	9.5 - 13	383	$1.2 \times 10^4$
Au (III)	Slight	Reaction	
Cu (I)	2 - 13	524	Unstable Colour

Figure 14. Spectral absorption curves of metal  
2,2' - diquinolyl ketoxime complexes.

1. Copper (II) complex in chloroform.
2. Nickel (II) complex in chloroform.
3. Cobalt complex in benzene.



FIGURE 14

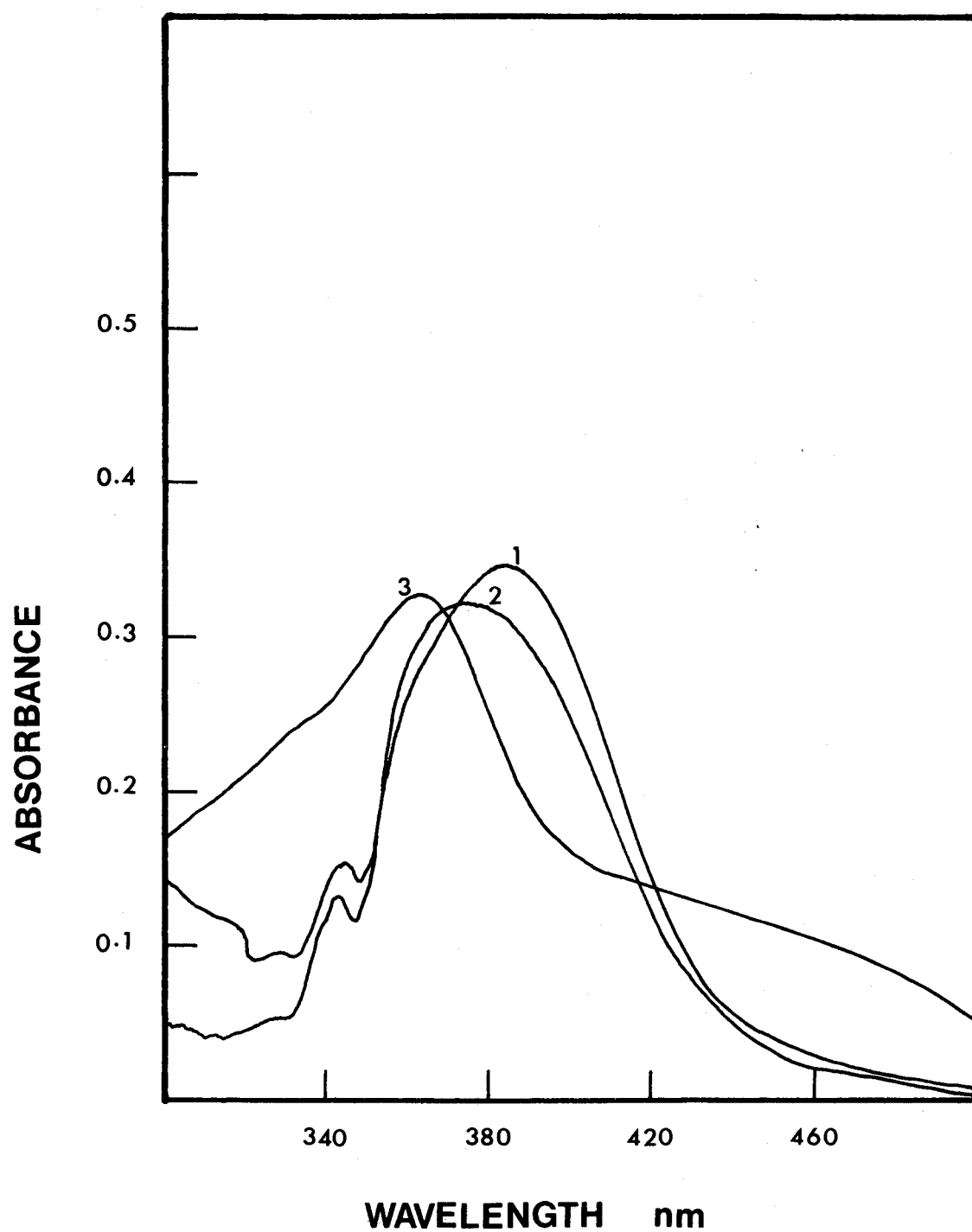
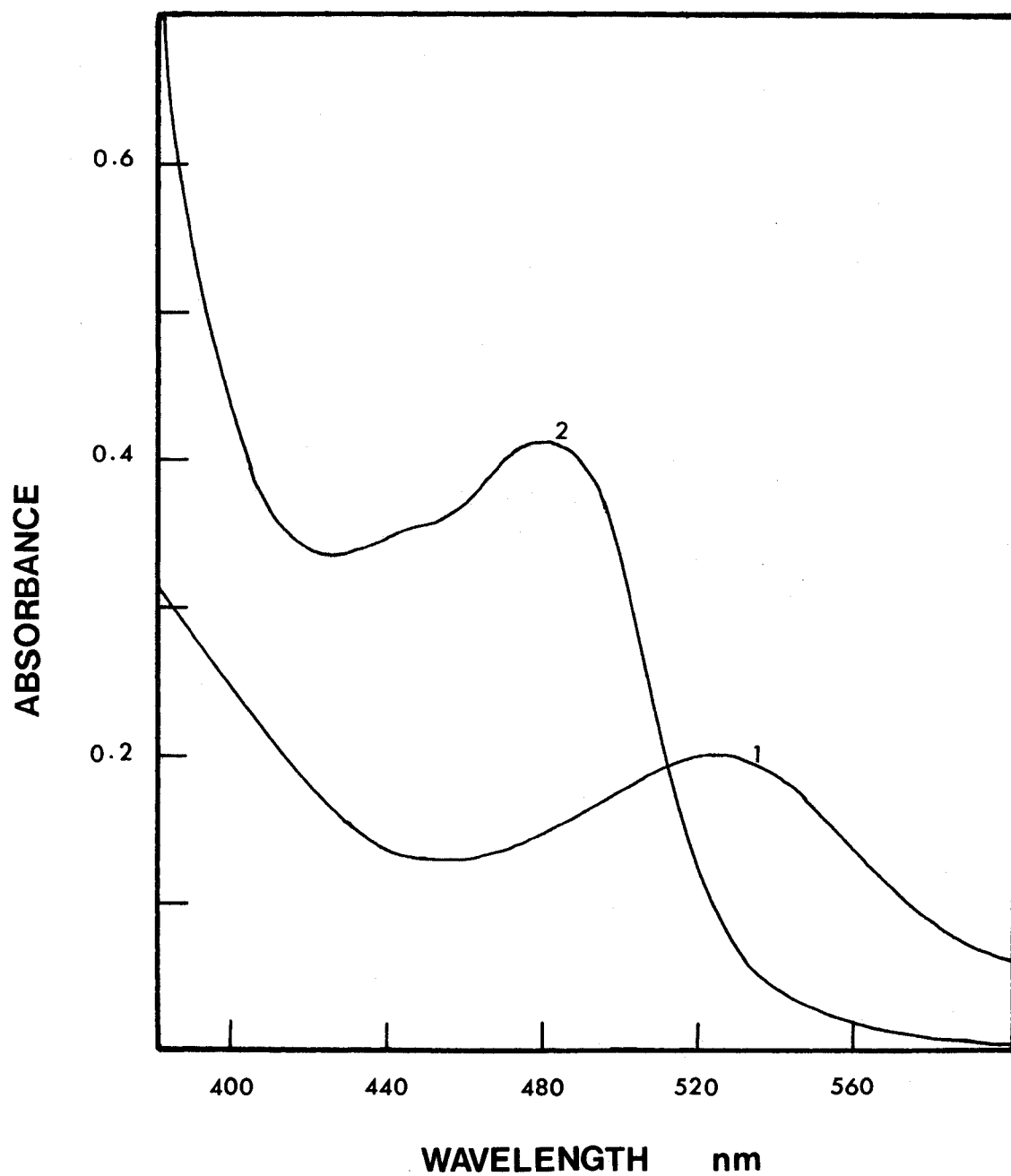


Figure 15. Spectral absorption curves of the copper (I) and palladium (II) complexes of 2,2' - diquinolyl ketoxime.

1. Copper (I) complex in benzene.
2. Palladium (II) complex in benzene.

FIGURE 15



The optimum pH for complex formation and extraction was 9.5 - 12.5. The molar absorptivity at 374 nm was  $1.15 \times 10^4$ . The complex was extractable into chloroform, benzene, methylene chloride, amyl alcohol and carbon tetrachloride. The colour of the organic extracts was stable for at least 12 hours.

2,2' - Diquinolyl ketoxime yielded a poor colour reaction with  $\text{Au}^{+3}$  and hence it was not investigated further.

The reagent reacted with  $\text{Pd}^{+2}$  over a wide pH range. The optimum pH range for complex formation and extraction was 6 - 13.5. The molar absorptivity was  $1.3 \times 10^4$  at 478 nm. The complex was extractable into the common organic solvents.

The reagent reacted with  $\text{Cu(II)}$  over the pH range 4 - 13.5. The optimum pH range for complex formation and extraction was 9.5 - 13. The molar absorptivity at the wavelength of maximum absorption (383 nm) was  $1.2 \times 10^4$ . The complex is extractable into chloroform and benzene and the colour of the organic extracts is stable for at least 24 hours.

The reagent formed a highly sensitive colour reaction with  $\text{Cu(I)}$ ; however, when the insoluble complex was extracted into an organic solvent the colour faded rapidly. After five minutes the colour was almost completely faded. Because of this difficulty the reaction of 2,2' - diquinolyl ketoxime with  $\text{Cu(I)}$  could not be further investigated.

Under strongly alkaline conditions the reagent reacted with cobalt to form a complex of high molar absorptivity. At the wavelength of maximum absorption (365 nm) the molar absorptivity was  $5.3 \times 10^4$ .

The cobalt complex was extractable into benzene, carbon tetrachloride, chloroform, methylene chloride and monochlorobenzene.

The reagent did not react with Fe(II) or Fe(III). This behaviour is analogous to the 1,10 - phenanthrolines with substituents at the 2 and 9 positions and with pyridine oximes having substituents at the 6 position.

#### D. SUMMARY AND CONCLUSIONS

The synthesis and properties of 2,2' - diquinolyl ketoxime have been described. The reagent formed coloured water - insoluble complexes with Ni(II), Cu(II), Cu(I), Au(III), Pd(II) and cobalt. A study of the various parameters indicated that the reagent could be applied to the spectrophotometric determination of cobalt and palladium.

## CHAPTER III

### SPECTROPHOTOMETRIC DETERMINATION OF COBALT

#### WITH 2,2' - DIQUINOLYL KETOXIME

##### A. INTRODUCTION

Many classes of reagents have been proposed for the spectrophotometric determination of cobalt. The most common reagents for cobalt contain the atomic grouping =  $\begin{array}{c} \text{NO} \\ | \\ \text{C} \end{array} - \begin{array}{c} \text{OH} \\ | \\ \text{C} \end{array} =$ . Many reagents containing this grouping have been proposed for the spectrophotometric determination of cobalt.

Ferroin reagents have found limited application as chromogens for cobalt. 2,2' - Dipyridyl ketoxime has been used for the spectrophotometric determination of cobalt (91). Recent studies on a series of ferroin reagents (96, 97), indicated them to be less sensitive than the classical reagents.

In the present work the ferroin reagent 2,2' - diquinolyl ketoxime was investigated as a new reagent for the spectrophotometric determination of cobalt. The reagent reacted with cobalt under strongly alkaline conditions to form an intensely coloured water-insoluble complex which was easily extractable into benzene.

Studies were undertaken to determine such factors as optimum concentration of reagent, effect of time of standing, influence of pH on complex formation and extraction, choice of solvent, effect of diverse ions and precision and accuracy. A procedure was developed for

the spectrophotometric determination of cobalt.

## B. EXPERIMENTAL

### 1) Instruments

Spectral studies and light absorption measurements were made with a Beckman DB spectrophotometer equipped with a Sargent Model - SRL recorder and 1.00-cm silica cells. A Sargent Model - DR pH meter was used for pH measurements.

### 2) Reagents

Standard cobalt solution: A stock solution was prepared by dissolving ultra-pure cobalt metal (Research Inorganic Chemical Corp., Sun Valley, California) in aqua regia, evaporating to near dryness and diluting to 1 liter with doubly distilled water. This was further diluted to give a standard solution of 2.215 ug/ml. Reagent solution: A 0.10% W/V solution in 95% ethanol was used. This solution was stable for at least 1 month.

Diverse cation solutions: Reagent grade chloride or nitrate salts were used. Arsenic, molybdenum, rhenium and selenium solutions were prepared from reagent grade sodium or potassium salts.

Benzene: A.C.S. grade was used.

### 3) Recommended Procedure

Add an aliquot of sample solution containing 3 - 20 ug of cobalt to a 50-ml beaker. After adjusting the volume to approximately 10 ml, either by evaporation on a hot plate or addition of distilled water, add 0.80 ml of reagent solution and adjust the pH to about 10 by the

dropwise addition of 10% potassium hydroxide solution. Add 10 ml of 2 M potassium hydroxide and extract with two 10-ml portions of benzene. Transfer the extracts to a 25-ml graduated glass -stoppered cylinder and make up to volume with benzene. Add 8 g of anhydrous sodium sulphate (to remove traces of water), shake and measure the absorbance of the clear solution at 365 nm against a reagent blank prepared in the same manner. The amount of cobalt is determined from a previously prepared calibration curve.

### C. RESULTS

#### 1) Effect of pH

The effect of pH is illustrated in Fig. 16. Highly alkaline conditions were required for complex formation and extraction. Reproducible results were obtained from pH 13.8 to 2 M KOH.

#### 2) Effect of Reagent Concentration

The reagent concentration must be kept at a minimum to avoid large blank readings. A volume of 0.80 ml of the reagent solution was sufficient for the optimum concentration range.

#### 3) Absorption Spectra

The benzene solution of the complex exhibited an absorption maximum at 365 nm. The reagent begins to absorb strongly near this wavelength (Fig. 17).

#### 4) Effect of Time

Complex formation was instantaneous under strong basic conditions and the benzene extracts were stable for 2 days.



Figure 16. Spectral curves of the cobalt 2,2' -  
diquinolyl ketoxime complex and the reagent blank extracted from  
aqueous solutions of varying pH.

1. pH = 8
2. pH = 9
3. pH = 10
4. pH = 11
5. pH = 12
6. pH = 13
7. pH = 13.5
8. pH = 14

FIGURE 16

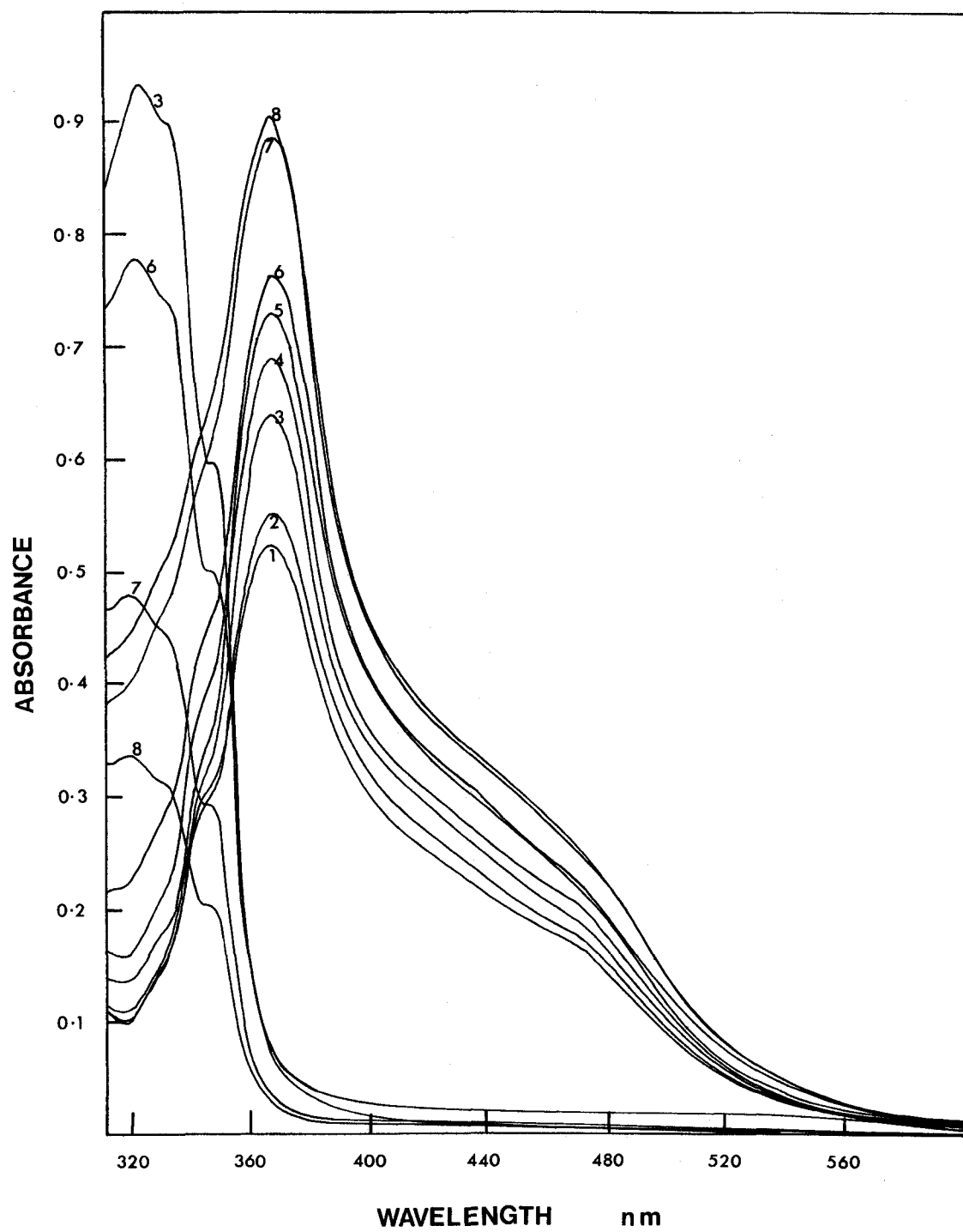
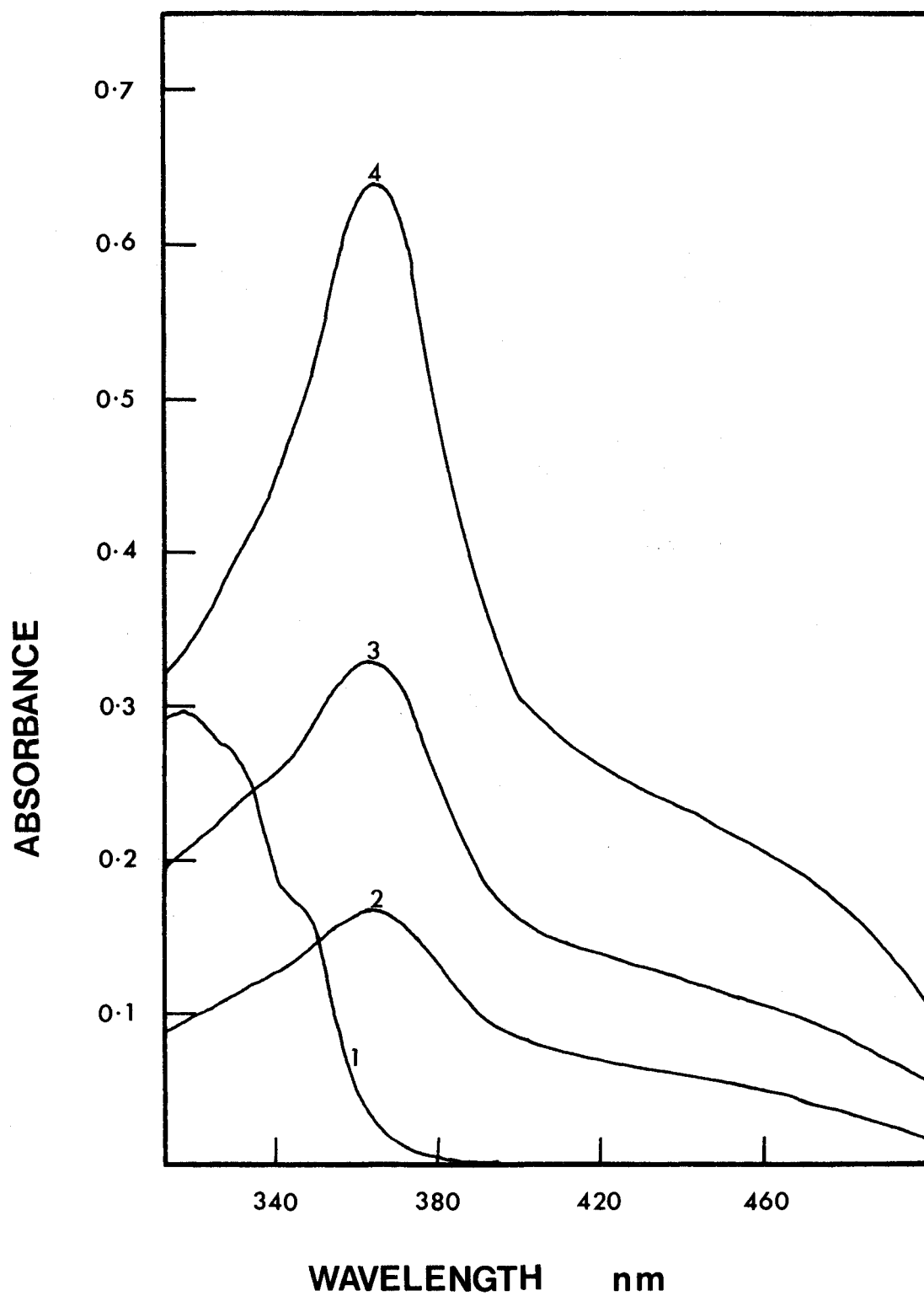


Figure 17. Spectral absorption curves of the cobalt 2,2' - diquinolyl ketoxime complex and the reagent blank extracted into benzene.

1. Reagent blank
2. 0.177 ppm cobalt
3. 0.354 ppm cobalt
4. 0.708 ppm cobalt

FIGURE 17



#### 5) Effect of Solvents

The complex was extractable into benzene, chloroform, methylene chloride, carbon tetrachloride, toluene and monochlorobenzene. Benzene gave the highest absorbance readings.

#### 6) Conformity to Beer's Law

Aliquots of cobalt solution of varying concentrations were analyzed using the recommended procedure. A Beer's Law plot at the absorption maxima of 365 nm was found to be linear over the range 0.10 - 1.20 ppm when 1.00-cm cells were used (Table XIV and Fig. 18). When 4.00-cm cells were used a straight line was obtained over the concentration range 0.04 - 0.18 ppm (Table XV and Fig. 19).

#### 7) Optimum Concentration Range

The optimum concentration range, evaluated from a Ringbom plot of the data in Table XVI, was found to be 0.22 - 0.89 ppm of cobalt as illustrated from the linear portion of the curve in Fig. 20.

#### 8) Sensitivity of the Method

The molar absorptivity at 365 nm was  $5.3 \times 10^4$ . The sensitivity of the method according to Sandell's definition was  $0.0011 \text{ ug cm}^{-2}$ .

#### 9) Precision and Accuracy

The precision and accuracy of the method was studied by analyzing solutions containing known amounts of cobalt. The results are summarized in Table XVII.

#### 10) Composition of the Cobalt Complex

Some of the complex was isolated, dried and analyzed. Cobalt, carbon, hydrogen and nitrogen analysis of the cobalt complex indicated

TABLE XIV  
DATA ON BEER'S LAW FOR THE SPECTROPHOTOMETRIC  
DETERMINATION OF COBALT WITH  
2,2' - DIQUINOLYL KETOXIME  
(Using 1.00-cm Cells)

Sample	Cobalt Concentration ppm	Absorbance
1	0.089	0.084
2	0.177	0.167
3	0.266	0.245
4	0.354	0.321
5	0.443	0.405
6	0.531	0.482
7	0.709	0.638
8	0.886	0.791
9	1.063	0.967
10	1.240	1.119
11	1.417	1.229

Figure 18. Beer's Law plot for the determination of cobalt with 2,2' - diquinolyl ketoxime using one-cm cells.

FIGURE 18

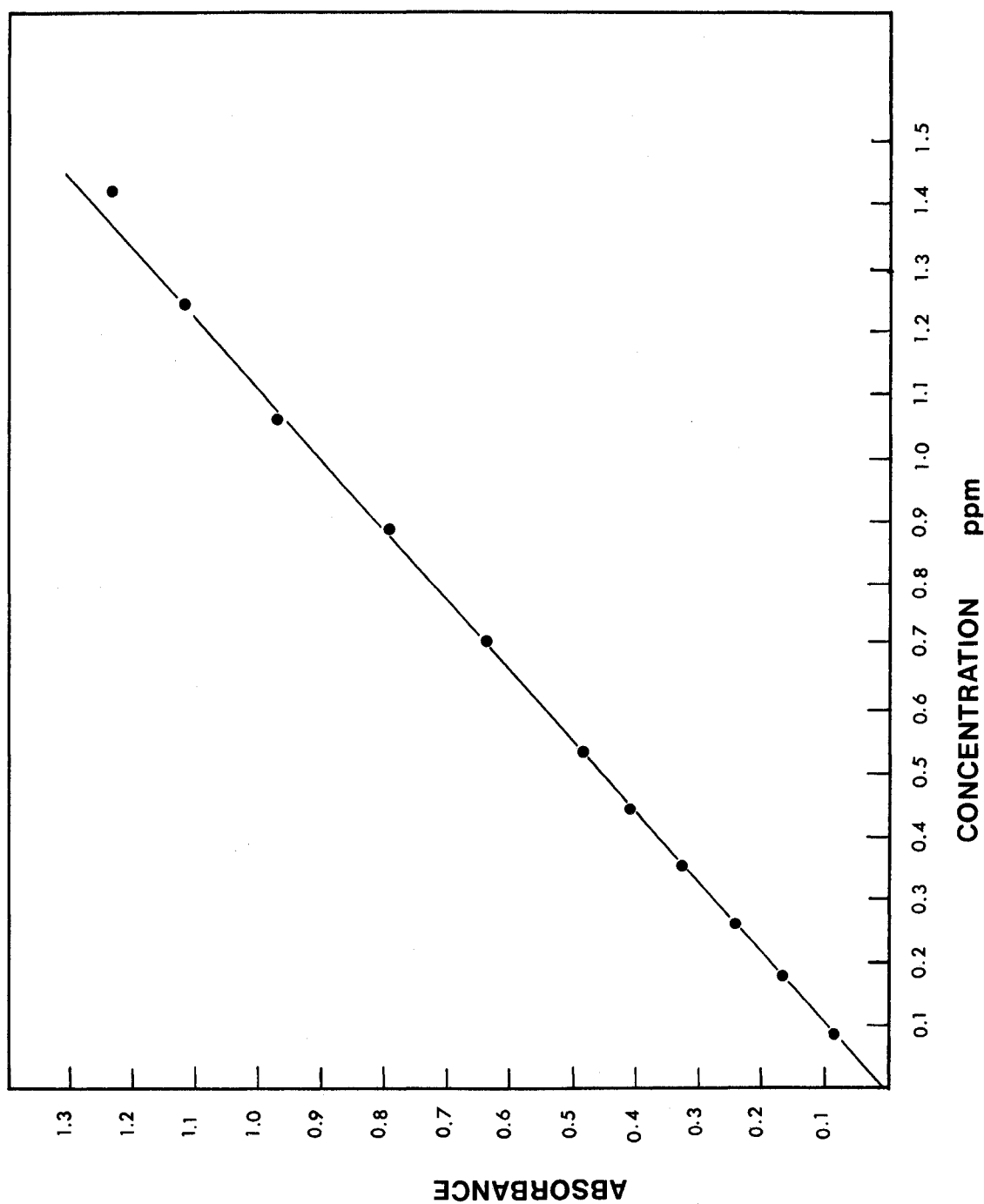




TABLE XV  
BEER'S LAW DATA USING 4.00-cm CELLS

Sample	Cobalt Concentration ppm	Absorbance
1	0.0222	0.068
2	0.0443	0.160
3	0.0665	0.228
4	0.0886	0.300
5	0.111	0.373
6	0.155	0.505
7	0.177	0.570
8	0.266	0.795

Figure 19. Beer's Law plot for the determination of cobalt with 2,2' - diquinolyl ketoxime using four-cm cells.

FIGURE 19

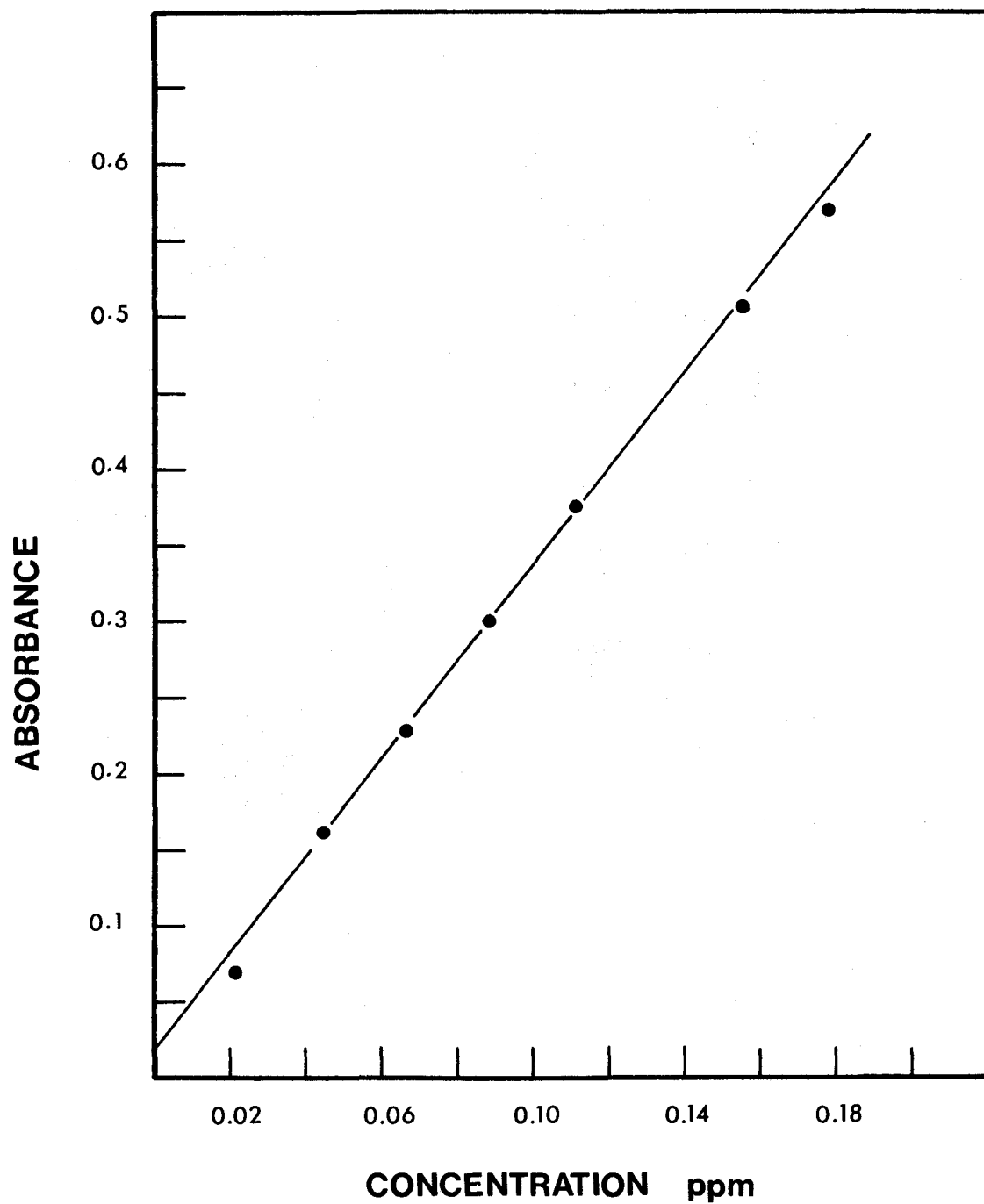


TABLE XVI  
RINGBOM DATA FOR THE DETERMINATION OF  
COBALT WITH 2,2' - DIQUINOLYL KETOXIME

Concentration ppm	Log c	% T	100 - T
0.089	-1.051	82.4	27.6
0.177	-0.752	68.3	31.7
0.266	-0.575	56.1	43.9
0.354	-0.451	47.7	52.3
0.443	-0.354	39.2	60.8
0.531	-0.275	33.0	67.0
0.709	-0.149	23.0	77.0
0.886	-0.053	16.2	83.8
1.063	0.027	10.8	89.2
1.240	0.093	7.6	92.4
1.417	0.151	5.9	94.1

Figure 20. Ringbom plot for the determination of cobalt with 2,2' - diquinolyl ketoxime.

FIGURE 20

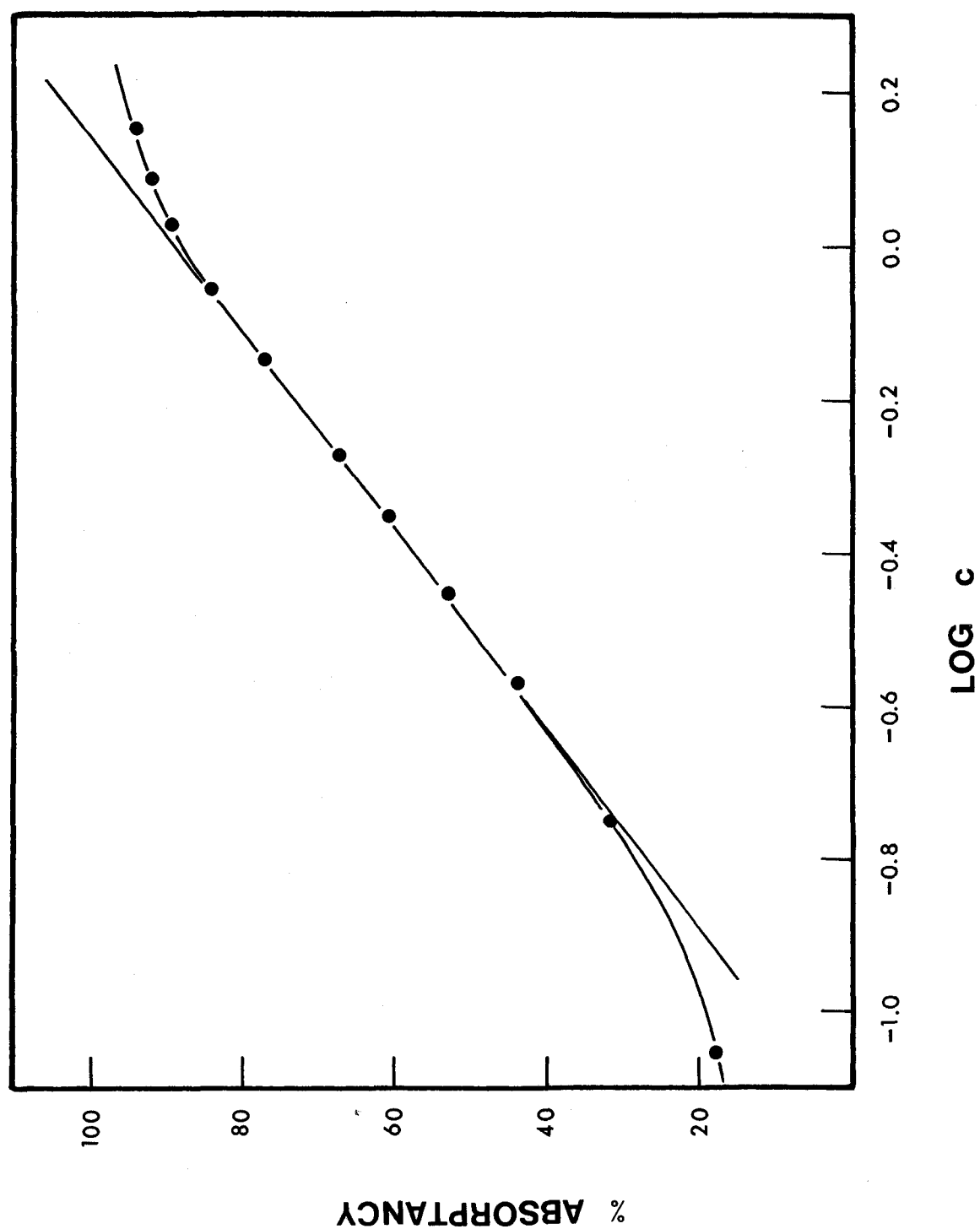


TABLE XVII  
PRECISION AND ACCURACY

Cobalt Taken ppm	Cobalt Found* ppm	Relative Error %	Standard Deviation	Range ppm
0.177	0.174	-1.69	0.003	0.010
0.354	0.352	-0.56	0.003	0.011
0.708	0.696	-1.13	0.007	0.024

\* Each result is the average of 16 separate analyses.

the presence of a 2:1 complex and a 3:1 complex. Attempts to purify the mixture were unsuccessful.

#### 11) Effect of Diverse Ions

Five mg of a diverse ion were added to a 50-ml beaker containing 8.86 ug of cobalt and the recommended procedure was followed. An error of 2% in the absorbance reading was considered tolerable. The following ions did not interfere:  $\text{Sr}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Li}^{+}$ ,  $\text{K}^{+}$ ,  $\text{Na}^{+}$ ,  $\text{Sn}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Br}^{-}$ ,  $\text{I}^{-}$ ,  $\text{F}^{-}$ ,  $\text{NO}_3^{-}$ ,  $\text{SO}_4^{-2}$ ,  $\text{SO}_3^{-2}$ ,  $\text{C}_2\text{O}_4^{-2}$ ,  $\text{OAc}^{-}$ ,  $\text{P}_2\text{O}_7^{-4}$ ,  $\text{PO}_4^{-3}$ ,  $\text{CO}_3^{-2}$ ,  $\text{ClO}_3^{-}$ ,  $\text{ClO}_4^{-}$ ,  $\text{NO}_2^{-}$ ,  $\text{As}^{+3}$ ,  $\text{Mo}^{+6}$ ,  $\text{V}^{+3}$ ,  $\text{VO}_3^{-}$ ,  $\text{W}^{+6}$ ,  $\text{Te}^{+4}$ ,  $\text{Re}^{+7}$ ,  $\text{Sb}^{+3}$  and  $\text{Se}^{+4}$ . A tolerance limit of 1 mg was found for the following ions:  $\text{Ga}^{+3}$ ,  $\text{Pb}^{+2}$  and  $\text{Hg}^{+2}$ . Up to 6 ml of 10% sodium citrate can be added. The system could also tolerate 0.5 mg of  $\text{Bi}^{+3}$ ,  $\text{Re}^{+3}$ ,  $\text{Sn}^{+2}$ ,  $\text{Cr}^{+6}$ ,  $\text{Pt}^{+2}$  and 0.1 mg of  $\text{Be}^{+2}$ ,  $\text{Nb}^{+5}$ ,  $\text{Cd}^{+2}$  and  $\text{In}^{+3}$ . The interferences due to  $\text{Au}^{+3}$ ,  $\text{Pd}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Cu}^{+}$  and  $\text{Ag}^{+}$  were eliminated by prior extraction with dithizone (98). At pH 2, 1 mg of each of the ions was quantitatively extracted by three 20-ml portions of  $10^{-3}$  M dithizone in chloroform. The interferences due to  $\text{Fe}^{+3}$ ,  $\text{Hf}^{+4}$ ,  $\text{Ti}^{+4}$ ,  $\text{Zr}^{+4}$  and  $\text{Sn}^{+4}$  were eliminated by prior chloroform extraction of their cupferrates with a 6% aqueous solution of cupferron from 1.2 M hydrochloric acid (99). The following ions interfere:  $\text{Ni}^{+2}$ ,  $\text{CN}^{-}$ , EDTA,  $\text{Mn}^{+2}$ ,  $\text{Cr}^{+3}$ , tartrate,  $\text{Ir}^{+3}$ ,  $\text{Ru}^{+3}$ ,  $\text{Rh}^{+3}$ ,  $\text{Mg}^{+2}$ ,  $\text{Ce}^{+3}$ ,  $\text{Ta}^{+5}$  and  $\text{Os}^{+8}$ .

#### D. DISCUSSION

In the present work, 2,2' - diquinolyl ketoxime has been applied to the spectrophotometric determination of cobalt. The procedure has the advantages of simplicity, rapidity, and a tolerance to many foreign



ions. Most metals commonly associated with cobalt either do not interfere or can be easily separated.

The main advantage of the present system is the extreme sensitivity. Using 4.00-cm cells, less than 0.1 ppm of cobalt can be easily determined. In Table XVIII a list of the sensitivities of some methods for cobalt is presented. It is readily apparent that 2,2' - diquinolyl ketoxime is more sensitive than the established reagents.

#### E. SUMMARY AND CONCLUSIONS

The spectrophotometric determination of cobalt involved the extraction of 3 - 20 ug of cobalt as a complex with 2,2' - diquinolyl ketoxime. The benzene extraction was performed from 1 - 2 M potassium hydroxide. The absorbance of the benzene extract was measured at 365 nm, the wavelength of maximum absorption of the complex and at this wavelength there was only slight absorption due to the excess reagent. The amount of cobalt was calculated from a previously prepared calibration curve.

Various parameters such as influence of pH on complex formation and extraction, effect of reagent, effect of time, choice of solvent, applicability of Beer's Law and foreign ions were studied. The optimum concentration range of 0.22 - 0.89 ppm of cobalt, evaluated by Ringbom's method, indicated the method to be extremely sensitive. Determinations of known amounts of cobalt showed the procedure to be both accurate and precise. The benzene extract of the complex was stable for 2 days. An extensive foreign ion study showed the procedure to be widely applicable.

TABLE XVIII  
SENSITIVITIES OF SOME METHODS FOR COBALT

Reagent	Sandell Sensitivity ug Co cm <sup>-2</sup>
2,2' - Diquinolyl Ketoxime	0.0011
Nitroso - R salt	0.0019
O - Nitrosoresorcinol	0.0025
2,2' - Dipyridyl Ketoxime	0.0029
2 - Nitroso - 1 - naphthol - 4 - sulfonic acid	0.004
2 - Nitroso - 1 - naphthol ( CHCl <sub>3</sub> )	0.0042

An abstracted portion of this section of work has previously been accepted for publication (100).

## CHAPTER IV

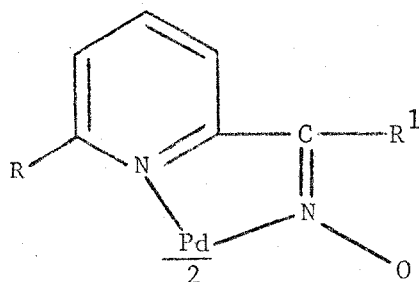
### SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

#### WITH 2,2' - DIQUINOLYL KETOXIME

##### A. INTRODUCTION

Because of their selectivity, oximes have been widely used as gravimetric and spectrophotometric reagents for palladium. Various vicinal dioximes have been extensively studied and applied to the determination of palladium. Recently, pyridine oximes containing the ferriox atomic grouping have been studied as spectrophotometric reagents for palladium.

Palladium has been determined by Pflaum, Wehking and Gensen (101) using 2 - pyridinealdoxime. Phenyl - 2 - pyridyl ketoxime was used by Sen (85) for the determination of palladium. The reagents 2,2' - dipyridyl ketoxime (90) and quinoline - 2 - aldoxime (102) have also been used for the determination of palladium. This class of reagents forms water-insoluble complexes with palladium (II) in which bonding between the pyridine nitrogen and oxime nitrogen is postulated (90, 103). The structure of the resulting five membered chelate may be represented as follows:



In the present work, 2,2' - diquinolyl ketoxime was investigated as a new reagent for the spectrophotometric determination of palladium. The reaction between palladium (II) and 2,2' - diquinolyl ketoxime was investigated to determine such factors as optimum concentration of reagent, influence of pH on complex formation and extraction, choice of solvent, effect of diverse ions and precision and accuracy. A procedure was developed for the spectrophotometric determination of palladium.

## B. EXPERIMENTAL

### 1) Apparatus

Spectral studies and light absorption measurements were made with a Beckman DB spectrophotometer equipped with a Sargent Model - SRL recorder and 1.00-cm silica cells. A Sargent Model - DR pH meter was used for pH measurements.

### 2) Reagents

Standard palladium solution: A stock solution of palladium (II) was prepared from pure palladium wire (Chapter II). This was further diluted to give a standard palladium solution of 27.46 ug/ml.

Reagent solution: A 0.30% W/V solution in 95% ethanol was used. This solution was stable for at least 1 month.

Diverse cation solutions: Reagent grade chloride or nitrate salts were used. Arsenic, molybdenum, rhenium and selenium solutions were prepared from the corresponding oxides. Diverse anion solutions: These were prepared from reagent grade sodium or potassium salts.

Benzene: A.C.S. grade was used.

### 3) Recommended Procedure

Transfer an aliquot of the acidified sample solution containing 20 - 200 ug of palladium (II) to a 50-ml beaker. Add 3 ml of reagent solution and adjust the pH to approximately 2 by the addition of dilute potassium hydroxide solution. Add 10 ml of a 5% W/V solution of the disodium salt of EDTA and adjust the pH to 6. Extract with two 10 ml portions of benzene and transfer the extracts to a 25-ml graduated glass - stoppered cylinder and make up to volume with benzene. Add 5 g of anhydrous sodium sulphate, shake and measure the absorbance of the clear solution at 478 nm against a reagent blank prepared in the same manner. The amount of palladium is determined from a previously prepared calibration curve.

### C. RESULTS

#### 1) Effect of pH

The optimum pH range for complex formation and extraction was 6 - 13.5 (Table XIX). The complex formed under strongly acidic conditions but the extraction was incomplete. The reagent was always added under acidic conditions to prevent the hydrolysis of palladium when the pH was adjusted to 6.

#### 2) Absorption Spectra

The benzene solution of the complex exhibited absorption maxima at 478 and 363 nm. The 478 nm maximum was chosen for analytical use since the reagent does not absorb at this wavelength (Fig. 21).

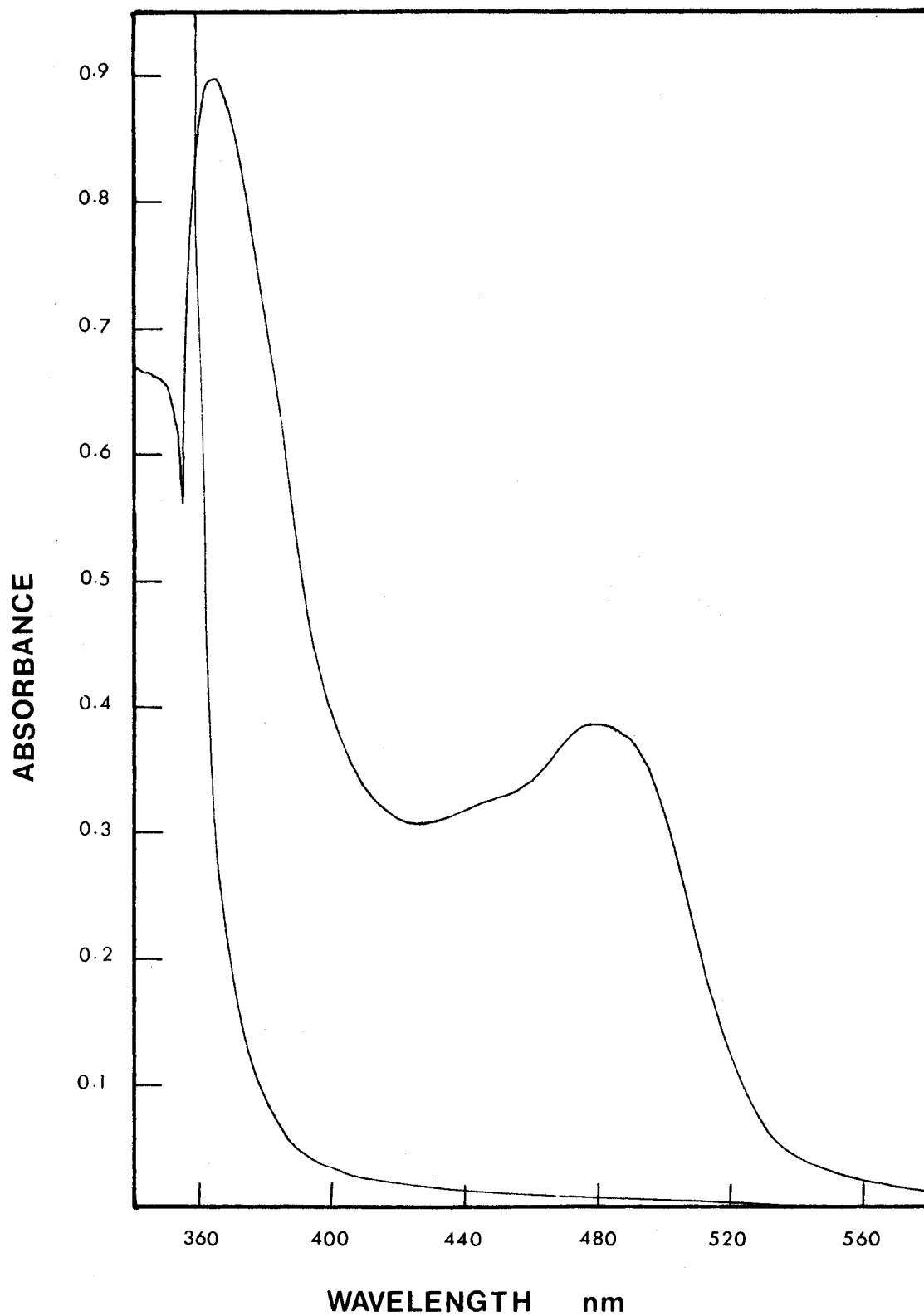
TABLE XIX  
EFFECT OF pH ON COMPLEX FORMATION AND EXTRACTION  
(3.30 ppm Palladium)

Sample	pH	Absorbance 478 nm
1	3.54	0.398
2	4.15	0.398
3	5.91	0.407
4	6.30	0.408
5	7.43	0.410
6	11.90	0.410
7	13.50	0.409

Figure 21. Spectral absorption curves of the palladium 2,2' - diquinolyl ketoxime complex and the reagent blank extracted into benzene.



FIGURE 21



### 3) Effect of Reagent Concentration

It was found that at least a 10 - fold excess of reagent is required for satisfactory results.

### 4) Effect of Time

Chelate formation was complete in less than 5 minutes and the benzene extracts were stable for at least two days.

### 5) Effect of Solvents

Changes in both the absorption maximum and the molar absorptivity occurred when different solvents were used for the extraction (Fig. 22). The complex was extractable into benzene, carbon tetrachloride, methylene chloride, chloroform, amyl alcohol and toluene.

### 6) Conformity to Beer's Law

A straight line was obtained over the range 0.5 - 10 ppm when absorbance was plotted against concentration (Table XX and Fig. 23).

### 7) Optimum Concentration Range

The optimum concentration range evaluated by Ringbom's method was 2 - 8 ppm (Table XXI and Fig. 24).

### 8) Sensitivity of the Method

The molar absorptivity at 478 nm was  $1.3 \times 10^4$ . The sensitivity of the method according to Sandell's definition was  $.0081 \text{ ug cm}^{-2}$ .

### 9) Precision and Accuracy

The precision and accuracy of the method was studied by analyzing solutions containing known amounts of palladium. The results are summarized in Table XXII.

### 10) Composition of the Palladium Complex

Attempts to isolate the palladium complex in pure form proved

Figure 22. Spectral absorption curves of the palladium 2,2' - diquinolyl ketoxime complex extracted into various solvents.

1. Toluene
2. Benzene
3. Carbon tetrachloride
4. Chloroform
5. Methylene chloride
6. Amyl alcohol

FIGURE 22

123

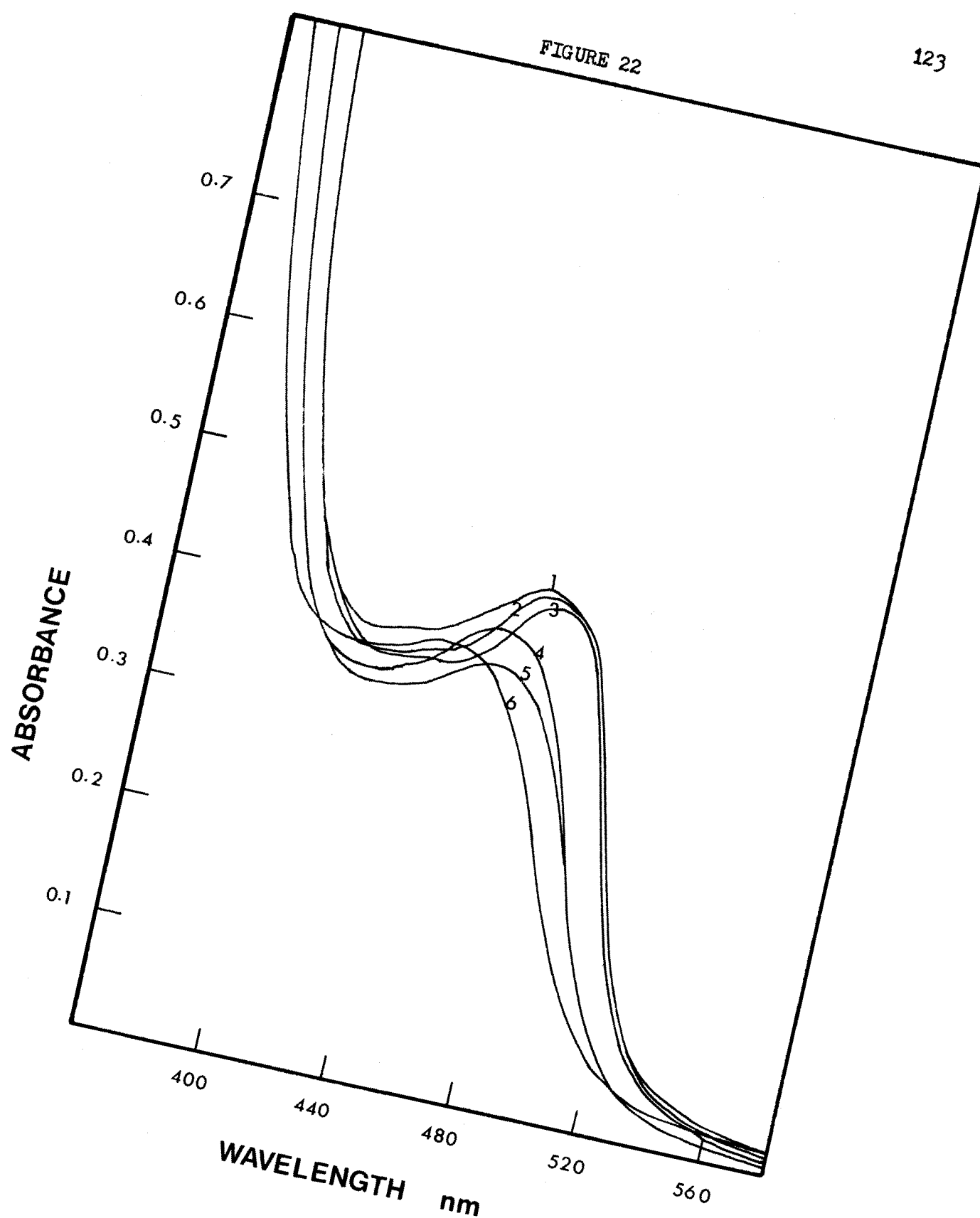


TABLE XX  
BEER'S LAW DATA FOR THE SPECTROPHOTOMETRIC  
DETERMINATION OF PALLADIUM WITH 2,2' - DIQUINOLYL KETOXIME

Sample	Palladium Concentration ppm	Absorbance
1	0.55	0.060
2	1.10	0.130
3	2.20	0.267
4	3.30	0.407
5	4.39	0.538
6	5.49	0.684
7	6.59	0.824
8	7.69	0.944
9	8.79	1.086
10	9.89	1.229

Figure 23. Beer's Law plot for the determination of palladium with 2,2' - diquinolyl ketoxime.

FIGURE 23

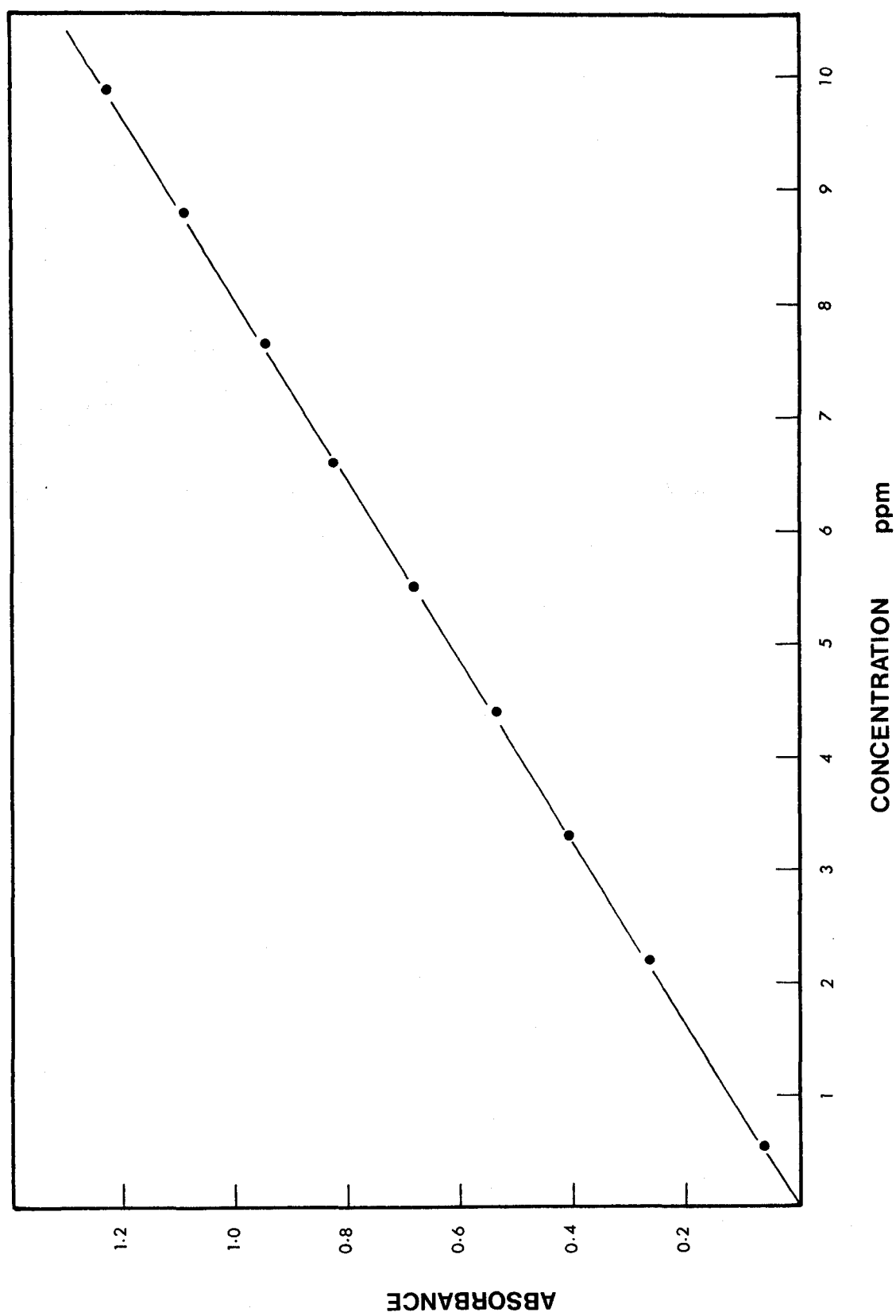


TABLE XXI  
RINGBOM DATA FOR THE DETERMINATION OF  
PALLADIUM WITH 2,2' - DIQUINOLYL KETOXIME

Concentration ppm	Log c	% T	100 - T
0.55	-0.260	87.2	12.8
1.10	0.041	74.2	25.8
2.20	0.342	54.1	45.9
3.30	0.519	39.2	60.8
4.39	0.643	29.0	71.0
5.49	0.740	20.7	79.3
6.59	0.819	15.0	85.0
7.69	0.886	11.4	88.6
8.79	0.944	8.2	91.8
9.89	0.995	5.9	94.1



Figure 24. Ringbom plot for the determination of palladium with 2,2' - diquinolyl ketoxime.

FIGURE 24

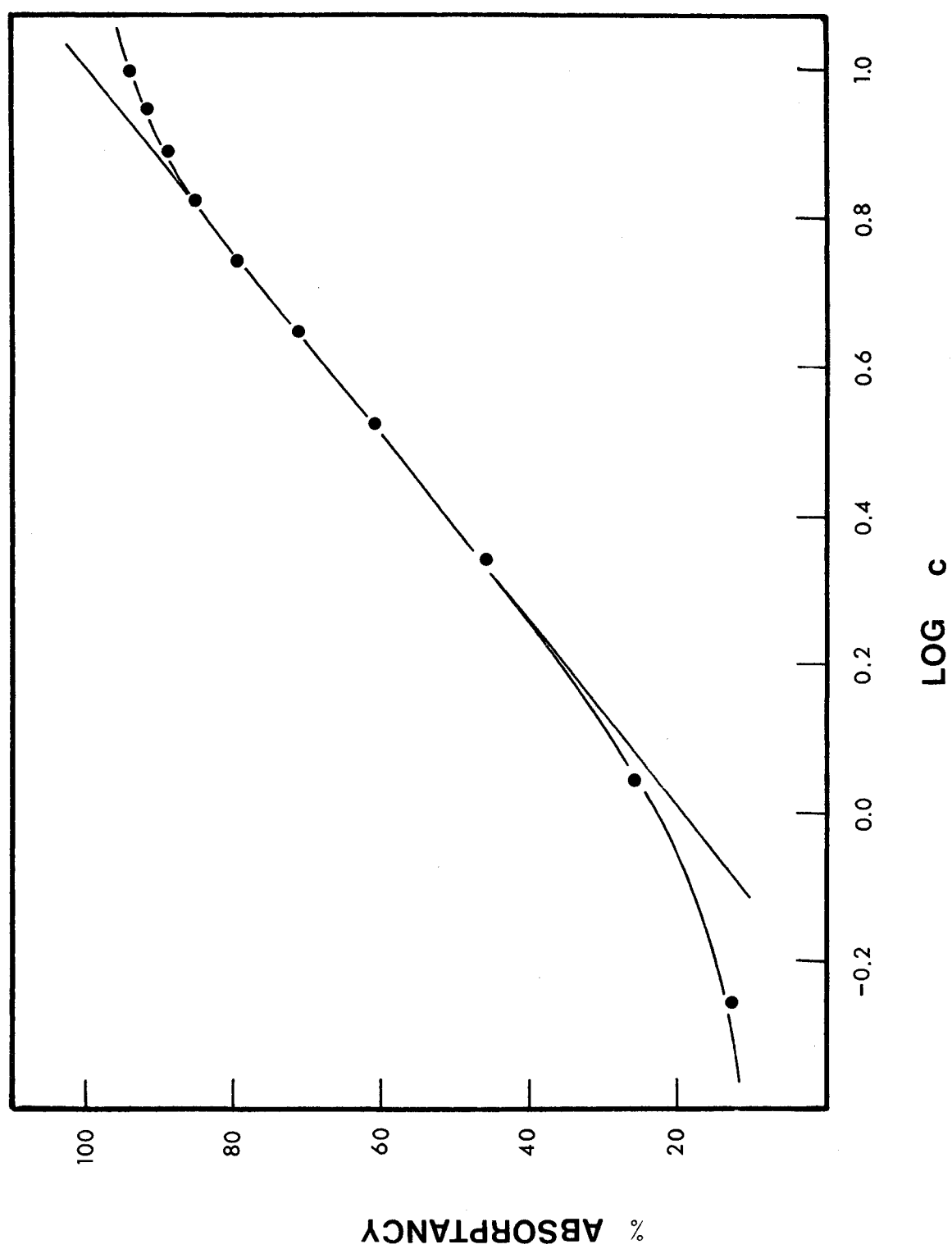


TABLE XXII  
PRECISION AND ACCURACY

Palladium Taken ppm	Palladium Found*	Relative Error %	Standard Deviation ppm	Range ppm
3.30	3.32	+0.61	0.044	0.15
2.20	2.18	-0.91	0.027	0.074
6.59	6.59	0.0	0.072	0.21

\* Each result is the average of 8 separate analyses.

unsuccessful.

#### 11) Effect of Diverse Ions

Five mg of a diverse ion were added to a 50-ml beaker containing 82.38 ug of palladium and the recommended procedure was followed. An error of 2% in the absorbance reading was considered tolerable. The following ions did not interfere:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Cl}^-$ ,  $\text{P}_2\text{O}_7^{4-}$ ,  $\text{Cd}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Tl}^+$ ,  $\text{F}^-$ ,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{Ni}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Ga}^{+3}$ ,  $\text{Hg}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{ClO}_3^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{OAC}^-$ ,  $\text{Ce}^{+3}$ ,  $\text{Pb}^{+2}$ ,  $\text{In}^{+3}$ ,  $\text{Se}^{+4}$ ,  $\text{Cr}^{+3}$ ,  $\text{Mn}^{+2}$ ,  $\text{As}^{+5}$ ,  $\text{Pt}^{+4}$ ,  $\text{UO}_2^{+2}$ ,  $\text{Cr}^{+6}$ ,  $\text{Be}^{+2}$  and  $\text{Mo}^{+6}$ . Large amounts of EDTA, citrate and tartrate can be tolerated. The system could also tolerate 2 mg of  $\text{Co}^{+2}$  and .5 mg of  $\text{Pt}^{+2}$ ,  $\text{Ir}^{+3}$ ,  $\text{Os}^{+8}$ ,  $\text{Rh}^{+3}$  and  $\text{Au}^{+3}$ . Only .1 mg of  $\text{Ru}^{+3}$  could be tolerated. The following ions did not interfere when used in conjunction with the appropriate masking agents: 2 mg of  $\text{Sn}^{+2}$  and  $\text{Sb}^{+5}$  masked with 100 mg of citrate; 2 mg of  $\text{Ti}^{+4}$ ,  $\text{Zr}^{+4}$ ,  $\text{Hf}^{+4}$  and  $\text{VO}_3^-$  can be masked with 50 mg  $\text{F}^-$ . The following ions interfere:  $\text{Sb}^{+3}$ ,  $\text{As}^{+3}$ ,  $\text{WO}_4^{2-}$ ,  $\text{I}^-$  and  $\text{Br}^-$ .

#### D. DISCUSSION

In the present work, a procedure was developed for the spectrophotometric determination of bivalent palladium based on the formation of an intensely coloured complex with 2,2' - diquinolyl ketoxime. The procedure has the advantages of simplicity, rapidity, and a tolerance to many foreign ions. The use of a large excess of EDTA incorporated in the method prevented the precipitation of metal hydroxides. Furthermore, EDTA formed stable complexes with a large number of ions and therefore

served as an excellent masking agent. Beer's Law was obeyed and there were no critical parameters to contend with.

The main advantages of the present system when compared to other systems using pyridine oximes are greater sensitivity and specificity. The sensitivities of various methods for palladium using pyridine oximes are compared in Table XXIII. The present system could tolerate relatively large amounts of gold. This is important since gold is commonly associated with palladium.

#### E. SUMMARY AND CONCLUSIONS

The spectrophotometric determination involved the extraction of the palladium - 2,2' - diquinolyl ketoxime complex from an aqueous solution of pH 6 - 13.5 into benzene and subsequent measurement of the organic extract at 478 nm.

A 0.30% W/V solution of 2,2' - diquinolyl ketoxime was used as the reagent solution.

Various parameters were investigated. The maximum colour intensity developed between a pH of 6 - 13.5. A large excess of reagent was used and no absorption due to reagent occurred at 478 nm. Chelate formation was complete in less than 5 minutes and the benzene extracts were stable for at least 2 days. The method obeyed Beer's Law over a wide concentration range and proved to be both precise and accurate. Furthermore, an extensive foreign ion study indicated that the procedure is widely applicable and most metals commonly associated with palladium do not interfere.

TABLE XXIII  
SENSITIVITIES OF SOME METHODS FOR  
PALLADIUM USING PYRIDINE OXIMES

Reagent	Molar Absorptivity $1 \text{ mole}^{-1} \text{ cm}^{-1}$	Sandell Sensitivity $\text{ug Pd cm}^{-2}$
2,2' - Diquinolyl Ketoxime	$1.3 \times 10^4$	0.0081
2,2' - Dipyridyl Ketoxime	$1.2 \times 10^4$	0.009
2 - Pyridinealdoxime	$1.0 \times 10^4$	0.0106
Phenyl - 2 - pyridyl ketoxime	$9 \times 10^3$	0.012

## CHAPTER V

### SUMMARY AND CONCLUSIONS

The reagent 2,2' - diquinolyl ketoxime has been synthesized and its properties were studied. A study of the reactions of metals with 2,2' - diquinolyl ketoxime indicated the reagent to be very sensitive and specific for cobalt and palladium.

Procedures were developed for the spectrophotometric determination of cobalt and palladium. The various parameters studied included the following; effect of pH, effect of reagent concentration, effect of time, effect of solvents, applicability of Beer's Law and the effect of diverse ions.

The sensitivity and specificity of the two procedures developed should make them the methods of choice for the analysis of trace amounts of cobalt and palladium in a wide variety of materials.

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